Syntheses of three menbers of $A^{(II)}M^{(IV)}(PO_4)_2$: Luminescence Properties of $PbGe(PO_4)_2$ and Its Eu^{3+}-doped Powders

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Electronic Supplementary Information (ESI)

Table S1 Crystal data and structural refinements for $PbGe(PO_4)_2$, $SrGe(PO_4)_2$, and $PbTi(PO_4)_2$

Chemical formula	$PbGe(PO_4)_2$	$SrGe(PO_4)_2$	$PbTi(PO_4)_2$
Formula weight	469.75	469.75	445.01
Crystal system	Monoclinic,	Monoclinic,	Monoclinic,
Space group	C2/c (No. 62)	C2/c (No. 62)	C2/c (No. 62)
a (Å)	16.48(3)	16.170(13)	16.683(11)
b (Å)	5.068(8)	5.065(4)	5.171(3)
c (Å)	7.963(14)	7.869(7)	8.229(5)
β (°)	114.92(3)	115.072(13)	116.155(7)
V (Å3)	603.2(18)	583.8(8)	637.3(7)
Z	4	4	4
Dcalcd (g/cm^3)	5.173	3.984	4.639
μ(Mo Kα)/mm-1	33.395	33.395	28.148
Reflections collected	2149	2149	2214
Completeness to theta	100.0 %	99.6 %	97.0 %
Reflections (I>2σ(I))	682	665	711
T (K)	293	293	293
GOF on F2	1.055	1.136	1.026
R1, wR2 [I > 2σ(I)]a	0.0383, 0.0980	0.0238, 0.0578	0.0448, 0.1067
R1, wR2 (all data)	0.0397, 0.0994	0.0246, 0.0582	0.0496, 0.1094

$$^aR1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|, \ wR2 = \{\Sigma w[(Fo)^2 - (Fc)^2]^2/\Sigma w[(Fo)^2]^2\}^{1/2}$$

Table S2 Atomic coordinates (x10^4) and displacement parameters (Å^2 x 10^3) for PbGe(PO$_4$)$_2$, SrGe(PO$_4$)$_2$ and PbTi(PO$_4$)$_2$.

Atom	x	y	z	$U_{(eq)}{}^a$
PbGe(PO$_4$)$_2$				
Pb(1)	0	6847(1)	2500	18(1)
Ge(1)	2500	2500	0	7(1)
P(1)	1490(2)	2405(5)	2646(3)	8(1)
O(1)	2231(5)	2318(15)	1997(9)	10(1)
O(2)	1685(4)	4680(14)	4095(9)	11(1)
O(3)	1524(4)	9750(13)	3669(9)	10(1)
O(4)	552(5)	2805(15)	1176(10)	14(1)
SrGe(PO$_4$)$_2$				
Sr(1)	0	2140(1)	2500	11(1)
Ge(1)	2500	2500	5000	5(1)
P(1)	1471(1)	-2566(1)	2636(1)	5(1)
O(1)	521(2)	-2329(4)	1106(3)	12(1)
O(2)	1626(1)	-213(4)	4002(3)	8(1)
O(3)	3477(1)	159(4)	6261(3)	9(1)
O(4)	2253(2)	2617(3)	7049(3)	8(1)
PbTi(PO$_4$)$_2$				
Pb(1)	0	1744(2)	2500	21(1)
Ti(2)	-2500	-2500	5000	7(1)
P(1)	-1438(2)	-2616(6)	2418(4)	7(1)
O(1)	-1675(5)	-408(17)	1006(11)	12(2)
O(2)	1486(5)	4768(17)	3529(11)	11(2)
O(3)	-502(5)	-2110(19)	3870(11)	16(2)
O(4)	-2145(5)	-2667(18)	3132(12)	12(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table S3 Selected bond lengths (Å) and angles [deg] for PbGe(PO$_4$)$_2$, SrGe(PO$_4$)$_2$ and PbTi(PO$_4$)$_2$.

PbGe(PO$_4$)$_2$							
Pb1-O4	2.635(8)	Pb1-O4#1	2.635(8)	Pb1-O4#2	2.680(9)
Pb1-O4#3	2.680(9)	Pb1-O3	2.715(7)	Pb1-O3#1	2.715(7)
Pb1-O2#1	2.749(8)	Pb1-O2	2.749(8)		
Ge1-O1#5	1.825(7)	Ge1-O1	1.825(7)	Ge1-O2#6	1.885(7)
Ge1-O2#7	1.885(7)	Ge1-O3#6	1.890(7)	Ge1-O3#7	1.890(7)

P1-O4	1.510(8)	P1-O1	1.513(8)	P1-O3#8	1.562(7)
P1-O2	1.566(7)				
SrGe(PO$_4$)$_2$					
Sr1-O1#1	2.597(3)	Sr1-O1#2	2.597(3)	Sr1-O3#3	2.618(3)
Sr1-O3#4	2.618(3)	Sr1-O2#5	2.664(3)	Sr1-O2	2.664(3)
Sr1-O1#5	2.797(3)	Sr1-O1	2.797(3)	Sr1-O1#6	3.247(3)
Sr1-O1#7	3.247(3)				
Ge1-O4#3	1.819(3)	Ge1-O4	1.819(3)	Ge1-O3	1.886(2)
Ge1-O3#3	1.886(2)	Ge1-O2	1.887(2)	Ge1-O2#3	1.887(2)
P1-O1	1.501(2)	P1-O4#8	1.520(3)	P1-O2	1.552(2)
P1-O3#9	1.556(2)				
PbTi(PO$_4$)$_2$					
Pb1-O3#1	2.603(9)	Pb1-O3	2.603(9)	Pb1-O3#2	2.731(9)
Pb1-O3)#3	2.731(9)	Pb1-O2	2.731(9)	Pb1-O2#1	2.731(9)
Pb1-O1)	2.744(8)	Pb1-O1#1	2.744(8)		
Ti2-O4)#4	1.877(9)	Ti2-O4	1.877(9)	Ti2-O1#5	1.958(8)
Ti2-O1)#6	1.958(8)	Ti2-O2#7	1.974(8)	Ti2-O2#2	1.974(8)
P1-O3)	1.514(8)	P1-O4	1.532(9)	P1-O2#8	1.546(9)
P1-O1	1.551(9)				

Symmetry transformations used to generate equivalent atoms:

For PbGe(PO$_4$)$_2$: #1 -x,y,-z+1/2; #2 x,-y+1,z+1/2; #3 -x,-y+1,-z; #4 -x,-y+1,-z+1;   #5 -x+1/2,-y+1/2,-z; #6 x,-y+1,z-1/2; #7 -x+1/2,y-1/2,-z+1/2; #8 x,y-1,z; #9 -x+1/2,y+1/2,-z+1/2; #10 x,y+1,z;
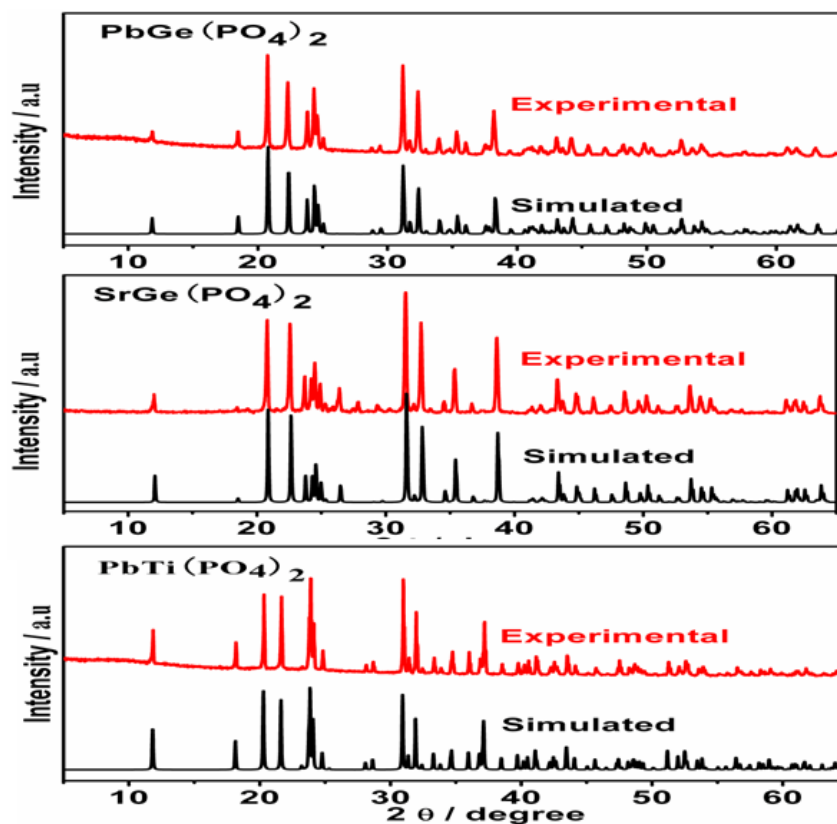
For SrGe(PO$_4$)$_2$: #1 x,-y,z+1/2; #2 -x,-y,-z; #3 -x+1/2,-y+1/2,-z+1; #4 x-1/2,-y+1/2,z-1/2; #5 -x,y,-z+1/2; #6 -x,y+1,-z+1/2; #7 x,y+1,z;   #8 x,-y,z-1/2;   #9 -x+1/2,-y-1/2,-z+1; #10 x,y-1,z;

For PbTi(PO$_4$)$_2$: #1 -x,y,-z+1/2; #2 -x,-y,-z+1; #3 x,-y,z-1/2; #4 -x-1/2,-y-1/2,-z+1; #5 -x-1/2,y-1/2,-z+1/2; #6 x,-y,z+1/2; #7 x-1/2,y-1/2,z; #8 -x,y-1,-z+1/2; #9 -x-1/2,y+1/2,-z+1/2;   #10 -x,y+1,-z+1/2;   #11 x+1/2,y+1/2,z;

Table S4 CIE Chromaticity Coordinates of Pb$_{1-x}$Eu$_x$Ge(PO$_4$)$_2$

Pb$_{1-x}$Eu$_x$Ge(PO$_4$)$_2$	λ_{ex} (nm)	λ_{em} (nm)	CIE
X=0	265 nm	Em$_{base}$ = broad-band(350-700)	(0.23,0.40)
X=0.02	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.22,0.36)
X=0.04	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.31,0.36)
X=0.06	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.35,0.36)
X=0.07	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.37,0.37)
X=0.08	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.43,0.37)
X=0.15	265 nm	Em$_{base}$, 594, 612, 653 and 700	(0.47,0.37)

Figure S1 Simulated a (black line) and experimental b (red line) powder X-ray (CuKa) diffraction patterns for $PbGe(PO_4)_2$, $SrGe(PO_4)_2$, and $PbTi(PO_4)_2$.

Figure S2 The coordination of oxygen atoms around Pb^{2+}. Pb, and O atoms are represented by teal and red, respectively.
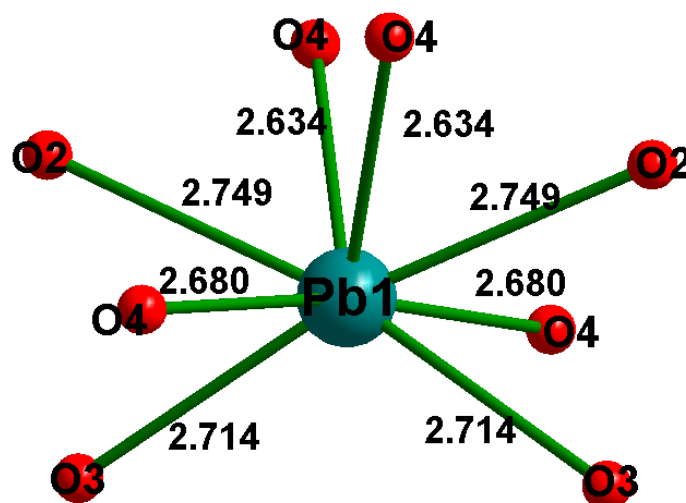
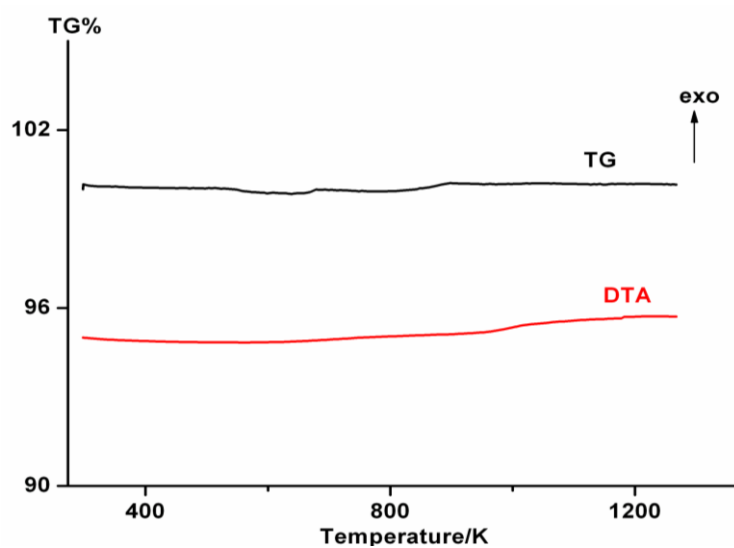**Figure S3** TGA and DTA curves for $PbGe(PO_4)_2$ from room temperature to 1273 K

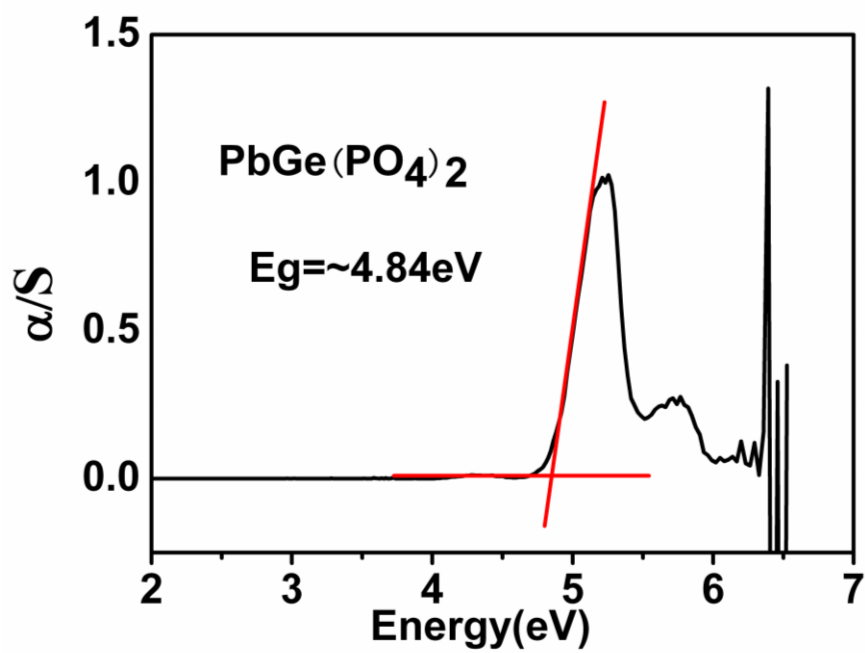**Figure S4** Optical diffuse reflectance spectra for $PbGe(PO_4)_2$.

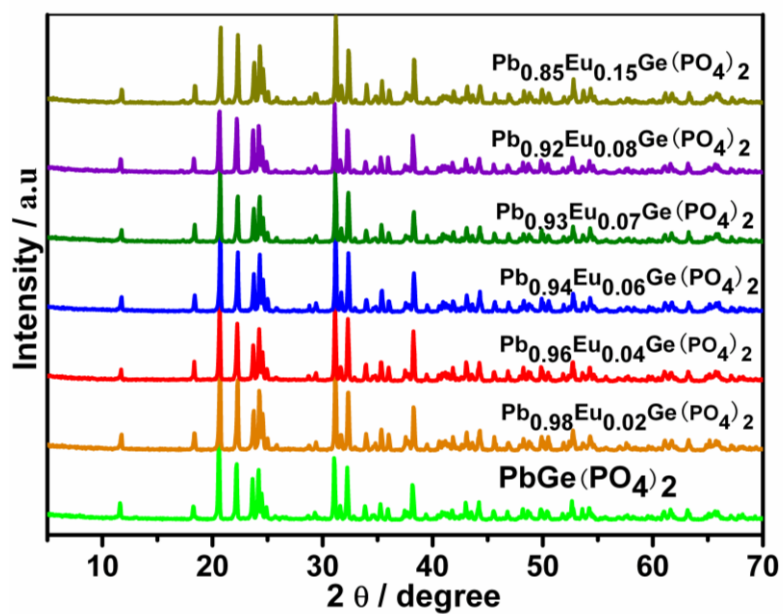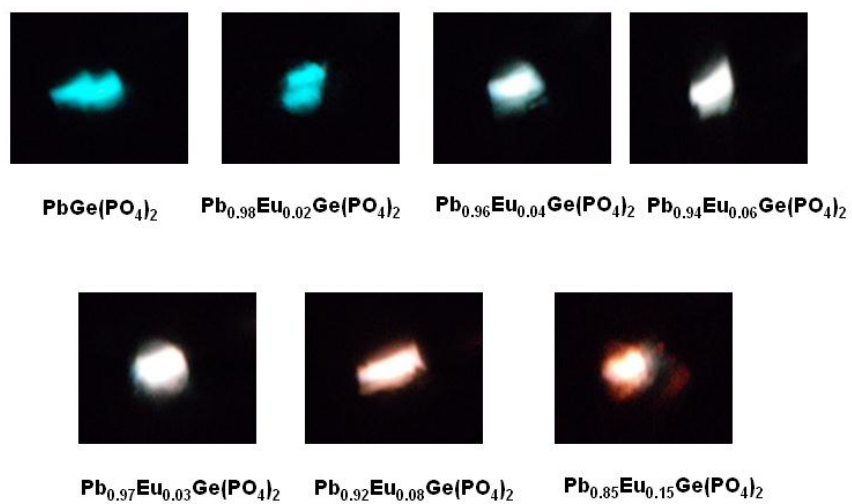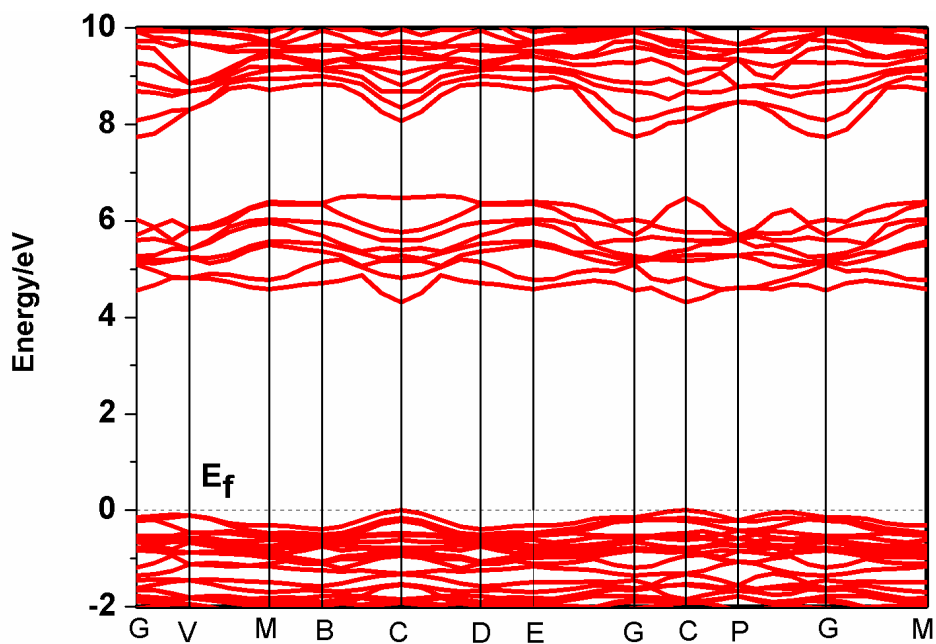**Figure S5** Powder X-ray (CuKa) diffraction patterns for $Pb_{1-x}Eu_xGe(PO_4)_2$

Figure S6 PL images of $PbGe(PO_4)_2$ and $Pb_{1-x}Eu_xGe(PO_4)_2$ samples excited by 265nm light.

PL Images of $Pb_{1-x}Eu_xGe(PO_4)_2$

Figure S7 The calculated band structures of $PbGe(PO_4)_2$ crystal in the range of -2.0 and 10.0 eV. The Fermi level is set at 0 eV.

Figure S8 PDOS of Eu in $PbGe(PO_4)_2$ with 6. 25% Eu^{3+}doping given by GGA+U. The Fermi level is set at 0 eV.