Supporting Information

The role of anionic heterovalent $[PO_4]^{3-} \rightarrow [GeO_4]^{4-}$ substitution on the luminescent properties in inorganic phosphors with the β-$Ca_3(PO_4)_2$ type structure: New data based on accurate crystal structure refinement

Dina V. Deyneko[1,2*], Ivan V. Nikiforov[1], Bogdan I. Lazoryak[1], Sergey M. Aksenov[2,3]

[1] *Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia*

[2] *Laboratory of Arctic Mineralogy and Material Sciences, Kola Science Centre, Russian Academy of Sciences, 14 Fersman str., Apatity 184209, Russia*

[3] *Geological Institute, Kola Science Centre, Russian Academy of Sciences, 14 Fersman Street, Apatity 184209, Russia*

[*] *Corresponding author: Chemistry Department, Moscow State University, 119991 Moscow, Russia.*

[*]Corresponding author: deynekomsu@gmail.com
Tel.: +74959393687
Fax.: +74959393316
E-mail: deynekomsu@gmail.ru
Chemistry Department, Moscow State University, Leninskie Gory 1, 119991 Moscow, Russia.

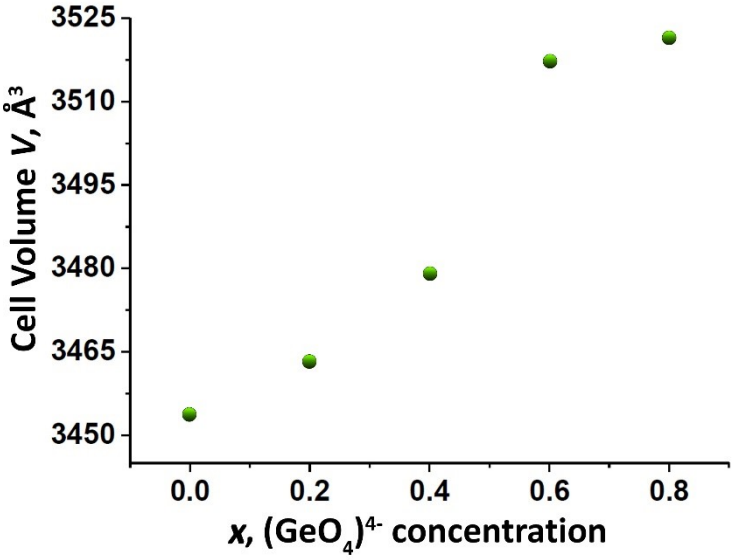

Fig. S1. The dependence of the cell volume V on the x, $(GeO_4)^{4-}$ concentration in $Ca_{8+0.5x}ZnEu(PO_4)_{7-x}(GeO_4)_x$.

Table S1. Main Crystallographic Data and experimental details for $Ca_{8.2}EuZn(PO_4)_{6.6}(GeO_4)_{0.4}$.

Phase	$Ca_{8.2}EuZnGe_{0.4}P_{6.6}O_{28}$
M_r	1227.4
Temperature, K	300
Crystal system, space group	Trigonal, *R*3*c*
a, *c* (Å)	10.38838(1), 37.22381(6)
V (Å^3)	3478.954(9)
Z	6
D_x (Mg m^{-3})	3.5152
Radiation type	Cu *K*α
Diffractometer	Rigaku SmartLab SE
θ-Range	2.5–40, step size (°) 0.02
R_{wp}	0.082
R_p	0.070
R_{Bragg}	0.051
S	2.54
No. of parameters	79

Table S2. Main Crystallographic Data and experimental details for $Ca_{8.3}EuZn(PO_4)_{6.4}(GeO_4)_{0.6}$.

Phase	$Ca_{8.3}EuZnGe_{0.6}P_{6.4}O_{28}$
M_r	1239.8
Temperature, K	300
Crystal system, space group	Trigonal, *R*3*c*
a, *c* (Å)	10.42877(3), 37.3433(1)
V (Å^3)	3517.321(9)
Z	6
D_x (Mg m^{-3})	3.5119
Radiation type	Cu *K*α
Diffractometer	Rigaku SmartLab SE
θ-Range	2.5–40, step size (°) 0.02
R_{wp}	0.089
R_p	0.083
R_{Bragg}	0.059
S	2.73
No. of parameters	79

Table S3. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{8.2}EuZn(PO_4)_{6.6}(GeO_4)_{0.4}$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso}	SOF
*M*1	18*b*	0.7154(1)	0.8307(3)	0.1724(6)	0.0113(6)	$Ca_{0.845(1)}Eu_{0.155(1)}$
*M*2	18*b*	0.6222(2)	0.8242(3)	–0.0295(8)	0.0113(6)	$Ca_{0.888(1)}Eu_{0.112(1)}$
*M*3	18*b*	0.7016(4)	0.8026(4)	0.0679(2)	0.0113(6)	$Ca_{0.934(1)}Eu_{0.066(1)}$
*M*4	6*a*	0	0	–0.0644(1)	0.0113(6)	$Ca_{0.20(1)}$
Zn1	6*a*	0	0	0.7369(6)	0.0113(6)	$Zn_{1.0}$
*T*1	6*a*	0	0	0.0061(5)	0.016(3)	$P_{1.0}$
*T*2	18*b*	0.6877(9)	0.8578(2)	0.8709 (4)	0.016(3)	$P_{1.0}$
*T*3	18*b*	0.6609(1)	0.8495(1)	0.7712(5)	0.016(3)	$P_{0.967(1)}Ge_{0.133(1)}$
O1	18*b*	0.7280(5)	0.8959(3)	0.9079(5)	0.011(3)	$O_{1.0}$
O2	18*b*	0.7493(1)	0.7619(3)	0.8585(6)	0.011(3)	$O_{1.0}$
O3	18*b*	0.7437(3)	1.0027(3)	0.8507(9)	0.011(3)	$O_{1.0}$
O4	18*b*	0.5296(1)	0.7706(7)	0.8666(6)	0.011(3)	$O_{1.0}$
O5	18*b*	0.6102(2)	0.9718(3)	0.7918(1)	0.011(3)	$O_{1.0}$
O6	18*b*	0.5904(3)	0.6856(3)	0.7852(7)	0.011(3)	$O_{1.0}$
O7	18*b*	0.8143(2)	0.9131(4)	0.7801(7)	0.011(3)	$O_{1.0}$
O8	18*b*	0.6285(5)	0.8277(4)	0.7278(7)	0.011(3)	$O_{1.0}$
O9	18*b*	0.0120(2)	0.8728(1)	–0.0203(4)	0.011(3)	$O_{1.0}$
O10	6*a*	0	0	0.0549(9)	0.011(3)	$O_{1.0}$

Table S4. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{8.3}EuZn(PO_4)_{6.4}(GeO_4)_{0.6}$.

Atom	Wyckoff site	*x*	*y*	*z*	U_{iso}	SOF
*M*1	18*b*	0.7191(6)	0.8281(3)	0.1681(3)	0.0113(6)	$Ca_{0.877(1)}Eu_{0.123(1)}$
*M*2	18*b*	0.6231(3)	0.8313(6)	–0.0285(1)	0.0113(6)	$Ca_{0.866(1)}Eu_{0.134(1)}$
*M*3	18*b*	0.6998(1)	0.8127(3)	0.0776(3)	0.0113(6)	$Ca_{0.923(1)}Eu_{0.077(1)}$
*M*4	6*a*	0	0	–0.0644(1)	0.0113(6)	$Ca_{0.30(1)}$
Zn1	6*a*	0	0	0.7355(7)	0.0113(6)	$Zn_{1.0}$
*T*1	6*a*	0	0	0.0066(6)	0.016(3)	$P_{1.0}$
*T*2	18*b*	0.6889(3)	0.8546(6)	0.8726(8)	0.016(3)	$P_{1.0}$
*T*3	18*b*	0.6582(2)	0.8449(6)	0.7734(9)	0.016(3)	$P_{0.800(1)}Ge_{0.200(1)}$
O1	18*b*	0.7254(4)	0.8812(1)	0.9099(7)	0.011(3)	$O_{1.0}$
O2	18*b*	0.7501(5)	0.7553(7)	0.8615(3)	0.011(3)	$O_{1.0}$
O3	18*b*	0.7453(5)	1.0069(7)	0.8561(3)	0.011(3)	$O_{1.0}$
O4	18*b*	0.5347(5)	0.7750(2)	0.8629(1)	0.011(3)	$O_{1.0}$
O5	18*b*	0.6102(2)	0.9718(3)	0.7918(4)	0.011(3)	$O_{1.0}$
O6	18*b*	0.5881(5)	0.6830(8)	0.7844(2)	0.011(3)	$O_{1.0}$
O7	18*b*	0.8132(6)	0.9138(4)	0.7839(1)	0.011(3)	$O_{1.0}$
O8	18*b*	0.6211(5)	0.8109(5)	0.7332(6)	0.011(3)	$O_{1.0}$
O9	18*b*	0.0120(2)	0.8728(4)	–0.0203(1)	0.011(3)	$O_{1.0}$
O10	6*a*	0	0	0.0548(9)	0.011(3)	$O_{1.0}$

Table S5. Selected bond length in the $Ca_{8.2}EuZn(TO_4)_{6.6}(GeO_4)_{0.4}$ structure.

*M*1–O2^{i}	2.808(4)	*M*4–O1^{x}	2.675(4)
*M*1–O3^{ii}	2.601(5)	*M*4–O1^{xi}	2.675(4)
*M*1–O4^{ii}	2.387(6)	*M*4–O1^{xii}	2.675(4)
*M*1–O4^{i}	2.518(7)	*M*4–O9^{xiii}	2.150(3)
*M*1–O5^{ii}	2.158(5)	*M*4–O9^{xiv}	2.150(3)
*M*1–O6^{i}	2.472(4)	*M*4–O9^{xv}	2.150(3)
*M*1–O8^{iii}	2.271(3)	<*M*4–O>	2.413
*M*1–O9^{iv}	2.673(2)	*M*5–O4^{xvi}	2.240(2)
<*M*1–O>	2.486	*M*5–O4^{xvii}	2.240(7)
*M*2–O1^{v}	2.524(2)	*M*5–O4^{xviii}	2.240(2)
*M*2–O2^{vi}	2.423(3)	*M*5–O7^{xix}	2.320(3)
*M*2–O3^{vii}	2.286(4)	*M*5–O7^{xx}	2.320(5)
*M*2–O5^{vii}	2.440(4)	*M*5–O7^{viii}	2.320(3)
*M*2–O6^{vi}	2.591(3)	<*M*5–O>	2.280
*M*2–O7^{vi}	2.425(5)	*T*1–O9^{xiii}	1.700(3)
*M*2–O7^{vii}	2.474(4)	*T*1–O9^{xiv}	1.700(3)
*M*2–O9^{viii}	2.222(2)	*T*1–O9^{xv}	1.700(3)
<*M*2–O>	2.423	*T*1–O10	1.816(4)
*M*3–O1^{vii}	2.777(3)	<*T*1–O>	1.729
*M*3–O2^{vi}	2.458(4)	*T*2–O1	1.436(2)
*M*3–O3^{vii}	2.485(3)	*T*2–O2	1.499(4)
*M*3–O5^{ii}	2.605(5)	*T*2–O3	1.514(3)
*M*3–O6^{i}	2.449(4)	*T*2–O4	1.433(7)
*M*3–O8^{ii}	2.507(5)	<*T*2–O>	1.471
*M*3–O8^{i}	2.673(5)	*T*3–O5	1.774(4)
*M*3–O10^{ix}	2.536(1)	*T*3–O6	1.569(3)
<*M*3–O>	2.562	*T*3–O7	1.426(2)
		*T*3–O8	1.644(3)
		<*T*3–O>	1.604

Symmetry codes: (i) –x+y+2/3,–x+4/3,z–2/3; (ii) –y+5/3,x–y+4/3,z–2/3; (iii) x,x–y+1,z–1/2; (iv) –y+4/3,–x+2/3,z+7/6; (v) x,y,z–1; (vi) –y+4/3,–x+5/3,z+1/6; (vii) –x+y+1/3,y–1/3,z+1/6; (viii) –x+y,–x+1,z; (ix) x+1,y+1,z; (x) x–1,y–1,z–1; (xi) –y+1,x–y,z–1; (xii) –x+y,–x+1,z–1; (xiii) x,y–1,z; (xiv) –y+1,x–y+1,z; (xv) –x+y–1,–x,z; (xvi) –y+2/3,–x+1/3,z–1/6; (xvii) –x+y–1/3,y–2/3,z–1/6; (xviii) x–1/3,x–y+1/3,z–1/6; (xix) x–1,y–1,z; (xx) –y+1,x–y,z

Table S6. Selected bond length in the $Ca_{8.3}EuZn(TO_4)_{6.4}(GeO_4)_{0.6}$ structure.

*M*1–O2^{i}	2.838(4)	*M*4–O1^{x}	2.666(4)
*M*1–O3^{ii}	2.657(6)	*M*4–O1^{xi}	2.666(9)
*M*1–O4^{ii}	2.329(8)	*M*4–O1^{xii}	2.666(4)
*M*1–O4^{i}	2.500(2)	*M*4–O9^{xiii}	2.160(3)
*M*1–O5^{ii}	2.161(1)	*M*4–O9^{xiv}	2.160(3)
*M*1–O6^{i}	2.483(2)	*M*4–O9^{xv}	2.160(3)
*M*1–O8^{iii}	2.495(8)	<*M*4–O>	2.413
*M*1–O9^{iv}	2.687(5)	*M*5–O4^{xvi}	2.337(7)
<*M*1–O>	2.519	*M*5–O4^{xvii}	2.341(2)
*M*2–O1^{v}	2.480(8)	*M*5–O4^{xviii}	2.337(7)
*M*2–O2^{vi}	2.430(1)	*M*5–O7^{xix}	2.476(8)
*M*2–O3^{vii}	2.444(1)	*M*5–O7^{xx}	2.476(4)
*M*2–O5^{vii}	2.519(7)	*M*5–O7^{viii}	2.476(8)
*M*2–O6^{vi}	2.565(9)	<*M*5–O>	2.408
*M*2–O7^{vi}	2.379(5)	*T*1–O9^{xiii}	1.719(4)
*M*2–O7^{vii}	2.486(2)	*T*1–O9^{xiv}	1.719(4)
*M*2–O9^{viii}	2.204(3)	*T*1–O9^{xv}	1.719(5)
<*M*2–O>	2.439	*T*1–O10	1.800(7)
*M*3–O1^{vii}	2.993(1)	<*T*1–O>	1.740
*M*3–O2^{vi}	2.330(1)	*T*2–O1	1.433(7)
*M*3–O3^{vii}	2.372(1)	*T*2–O2	1.521(1)
*M*3–O5^{ii}	2.584(8)	*T*2–O3	1.521(6)
*M*3–O6^{i}	2.442(1)	*T*2–O4	1.439(5)
*M*3–O8^{ii}	2.530(1)	<*T*2–O>	1.479
*M*3–O8^{i}	2.562(1)	*T*3–O5	1.772(7)
*M*3–O10^{ix}	2.520(3)	*T*3–O6	1.524(9)
<*M*3–O>	2.542	*T*3–O7	1.458(6)
		*T*3–O8	1.544(7)
		<*T*3–O>	1.575

Symmetry codes: (i) –x+y+2/3,–x+4/3,z–2/3; (ii) –y+5/3,x–y+4/3,z–2/3; (iii) x,x–y+1,z–1/2; (iv) –y+4/3,–x+2/3,z+7/6; (v) x,y,z–1; (vi) –y+4/3,–x+5/3,z+1/6; (vii) –x+y+1/3,y–1/3,z+1/6; (viii) –x+y,–x+1,z; (ix) x+1,y+1,z; (x) x–1,y–1,z–1; (xi) –y+1,x–y,z–1; (xii) –x+y,–x+1,z–1; (xiii) x,y–1,z; (xiv) –y+1,x–y+1,z; (xv) –x+y–1,–x,z; (xvi) –y+2/3,–x+1/3,z–1/6; (xvii) –x+y–1/3,y–2/3,z–1/6; (xviii) x–1/3,x–y+1/3,z–1/6; (xix) x–1,y–1,z; (xx) –y+1,x–y,z