Supporting Information

Influence of anionic substitutions on the nonlinear-optical and luminescent properties of $Ca_{9.75}Eu_{0.5}(VO_4)_7$.

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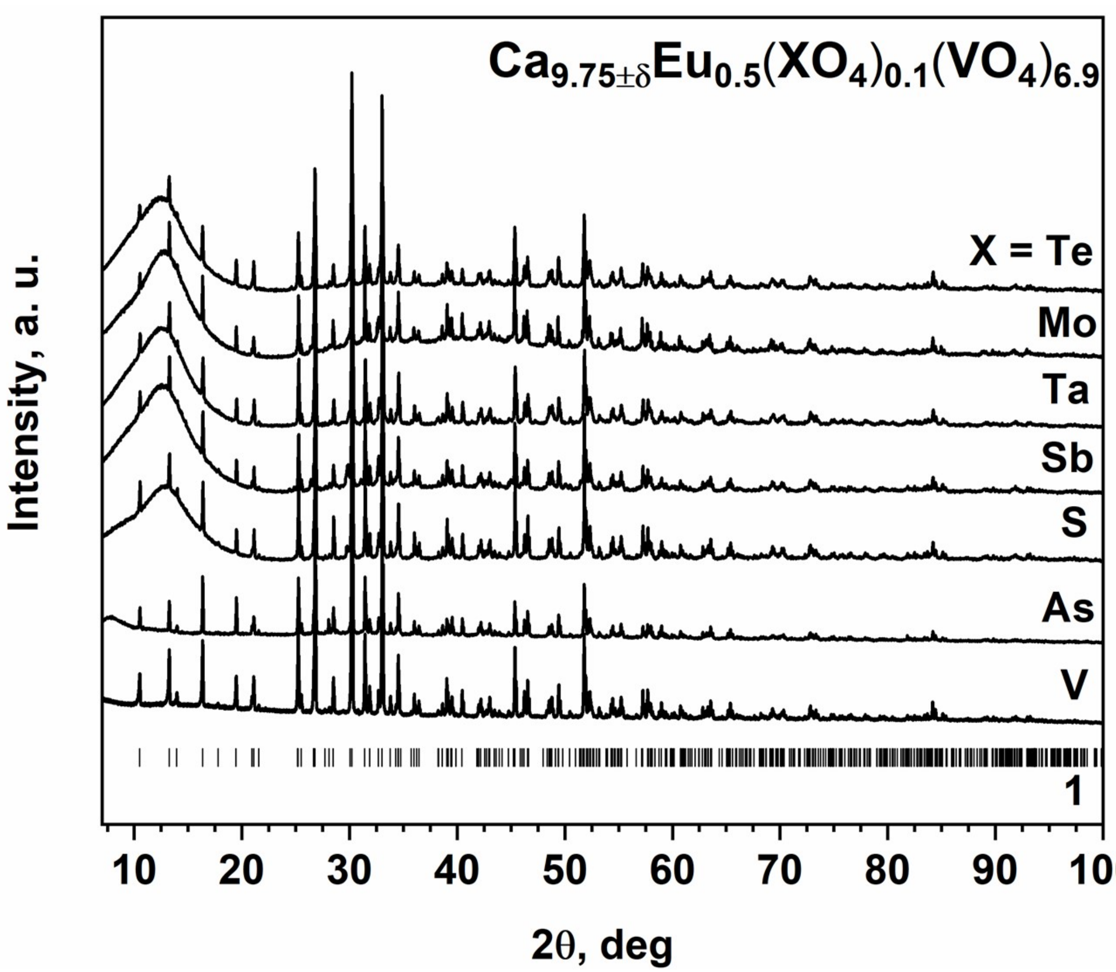


Fig. S1. X-ray diffraction patterns of $Ca_{9.75\pm\delta}Eu_{0.5}(XO_4)_{0.1}(VO_4)_{6.9}$ (X = As^{5+}, S^{6+}, Sb^{5+}, Ta^{5+}, Mo^{6+}, Te^{4+}, V^{5+}). 1 - Bragg reflections for $Ca_9Eu(VO_4)_7$ (PDF-2, No. 45-549).

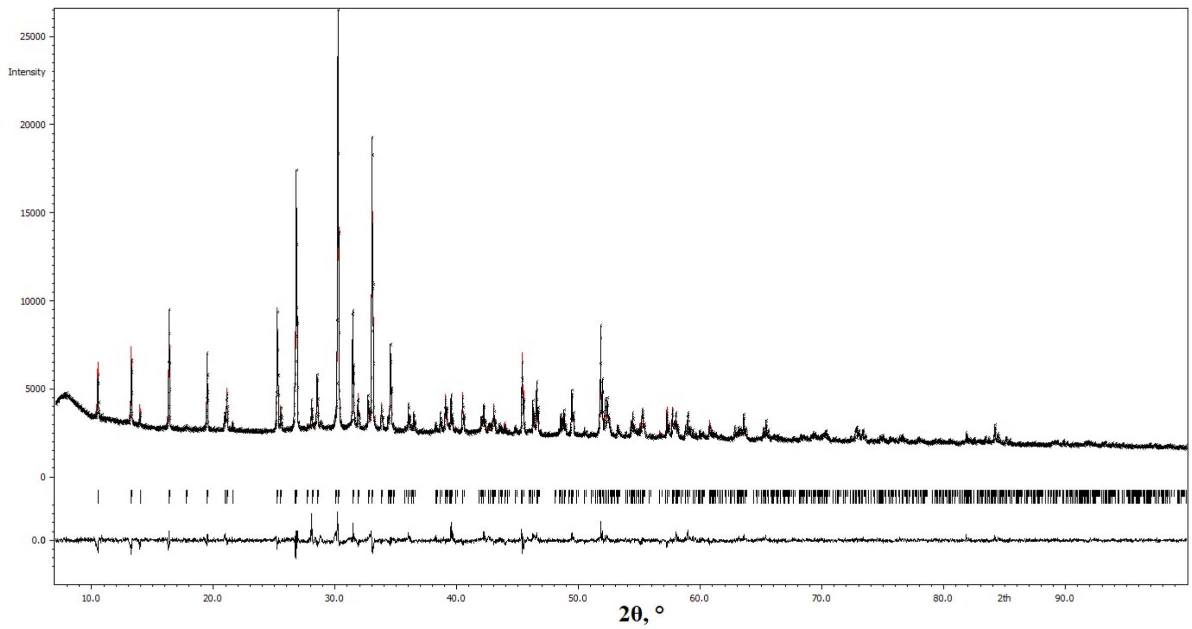


Fig. S2. Experimental, calculated, and difference XRD patterns for $Ca_{9.75\pm\delta}Eu_{0.5}(AsO_4)_{0.1}(VO_4)_{6.9}$. Bragg reflections are marked by short bars.

Table S1. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.862}Eu_{0.459}(TeO_4)_{0.1}(VO_4)_{6.9}$.

Atom	**Wyck.**	**S.O.F.**	***x***	***y***	***z***	**U [Å^2]**
Ca1	18b	0.89	0.1330(11)	0.2829(8)	0.1024(2)	0.003
Eu1	18b	0.11	0.1330(11)	0.2829(8)	0.1024(2)	0.003
Ca2	18b	0.98	0.5463(13)	0.4852(13)	0.0724(2)	0.011
Eu2	18b	0.02	0.5463(13)	0.4852(13)	0.0724(2)	0.011
Ca3	18b	0.98	0.2238(9)	0.3981(8)	0.0120(2)	0.014
Eu3	18b	0.02	0.2238(9)	0.3981(8)	0.0120(2)	0.014
Ca4	6a	0.32	0	0	-0.0248(15)	0.005
Ca5	6a	1	0.6666	0.3333	0.0051(5)	0.007
V1	6a	0.95	0	0	-0.0986(3)	0.011
Te1	6a	0.05	0	0	-0.0986(3)	0.011

V2	18b	1	0.3467(12)	0.1975(10)	0.1368(2)	0.014
V3	18b	0.98	0.3171(8)	0.1604(13)	0.0347(2)	0.005
Te3	18b	0.02	0.3171(8)	0.1604(13)	0.0347(2)	0.005
O11	6a	1	0	0	-0.1496(10)	0.002
O12	18b	1	0.1810(20)	0.5200(30)	0.0857(9)	0.012
O21	18b	1	0.4240(30)	0.1030(30)	0.1161(8)	0.006
O22	18b	1	0.3620(20)	0.1840(30)	0.1811(5)	0.004
O23	18b	1	0.4120(30)	0.3760(20)	0.1221(8)	0.001
O24	18b	1	0.1620(20)	0.0760(30)	0.1290(7)	0.002
O31	18b	1	0.2020(30)	-0.0180(20)	0.0419(8)	0.022
O32	18b	1	0.4900(20)	0.2470(40)	0.0475(6)	0.002
O33	18b	1	0.2390(20)	0.0710(20)	-0.0079(5)	0.003
O34	18b	1	0.2630(40)	0.2840(30)	0.0559(7)	0.006

Table S2. Selected distances (Å) in $Ca_{9.862}Eu_{0.459}(TeO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O$_8$	O12	2.44(3)
	O21	2.84(4)
	O23	2.77(3)
	O24	2.62(4)
	O24	2.43(3)
	O31	2.54(3)
	O33	2.61(2)
	O34	2.26(3)
	<M-O>	2.56
*M*2O$_8$	O12	2.40(4)
	O21	2.09(3)
	O22	2.36(3)
	O23	2.32(3)
	O31	3.27(3)
	O32	2.52(4)
	O32	2.36(4)
	O34	2.81(3)
	<M-O>	2.52
*M*3O$_9$	O11	2.54(1)
	O12	3.23(4)
	O21	2.65(3)
	O22	2.50(4)
	O22	2.93(4)

	O23	2.59(3)
	O31	2.38(2)
	O33	3.01(2)
	O34	2.24(4)
	<M-O>	2.67
*M*4O_6	O12	2.68(6)
	O12	2.68(6)
	O12	2.68(6)
	O33	2.39(3)
	O33	2.39(4)
	O33	2.39(3)
	<M-O>	2.54
*M*5O_6	O24	2.23(3)
	O24	2.23(4)
	O24	2.23(3)
	O32	2.31(3)
	O32	2.31(4)
	O32	2.31(3)
	<M-O>	2.27
V1O_4	O11	1.94(4)
	O12	1.76(2)
	O12	1.76(2)
	O12	1.76(2)
V2O_4	O21	1.80(4)
	O22	1.71(2)
	O23	1.79(3)
	O24	1.78(2)
V3O_4	O31	1.72(2)
	O32	1.69(2)
	O33	1.86(2)
	O34	1.89(4)

Table S3. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.718}Eu_{0.521}(TaO_4)_{0.1}(VO_4)_{6.9}$.

Atom	Wyck.	S.O.F.	*x*	*y*	*z*	U [Å^2]
Ca1	18b	0.88	0.1240(13)	0.2793(10)	0.0996(2)	0.001
Eu1	18b	0.12	0.1240(13)	0.2793(10)	0.0996(2)	0.001
Ca2	18b	0.94	0.5330(16)	0.4823(15)	0.0686(2)	0.002
Eu2	18b	0.06	0.5330(16)	0.4823(15)	0.0686(2)	0.002
Ca3	18b	1	0.2186(12)	0.3938(11)	0.0108(3)	0.001
Ca4	6a	0.24	0	0	-0.0223(18)	0.008
Ca5	6a	1	0.6666	0.3333	-0.0032(6)	0.007
V1	6a	1	0	0	-0.0988(4)	0.001
V2	18b	1	0.3516(13)	0.1996(11)	0.1342(3)	0.002

V3	18b	0.97	0.3204(8)	0.1691(15)	0.0328(2)	0.001
Ta3	18b	0.03	0.3204(8)	0.1691(15)	0.0328(2)	0.001
O11	6a	1	0	0	-0.1466(7)	0.0172
O12	18b	1	-0.1350(30)	0.0210(40)	-0.0796(9)	0.004
O21	18b	1	0.4820(30)	0.1540(30)	0.1183(10)	0.001
O22	18b	1	0.3700(20)	0.1830(40)	0.1819(6)	0.001
O23	18b	1	0.4020(30)	0.3860(20)	0.1218(10)	0.001
O24	18b	1	0.1660(20)	0.0720(40)	0.1315(8)	0.005
O31	18b	1	0.2380(30)	-0.0160(30)	0.0437(9)	0.005
O32	18b	1	0.4960(20)	0.2480(50)	0.0465(8)	0.008
O33	18b	1	0.1990(20)	0.0470(30)	-0.0059(6)	0.001
O34	18b	1	0.2560(30)	0.2680(30)	0.0571(7)	0.001

Table S4. Selected distances (Å) in $Ca_{9.718}Eu_{0.521}(TaO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O_8	O12	2.26(5)
	O21	3.38(4)
	O23	2.77(4)
	O24	2.78(4)
	O24	2.40(3)
	O31	2.38(3)
	O33	3.01(2)
	O34	2.20(4)
	<M-O>	2.65
*M*2O_8	O12	2.59(5)
	O21	2.32(4)
	O22	2.20(3)
	O23	2.39(4)
	O31	2.90(3)
	O32	2.51(6)
	O32	2.42(6)
	O34	2.76(3)
	<M-O>	2.51
*M*3O_9	O11	2.60(1)
	O12	3.22(4)
	O21	2.54(4)
	O22	2.45(5)
	O22	2.92(5)
	O23	2.56(4)
	O31	2.31(3)
	O33	2.83(3)
	O34	2.38(4)
	<M-O>	2.65

*M*4O_6	O12	2.70(7)
	O12	2.70(7)
	O12	2.70(7)
	O33	2.06(3)
	O33	2.06(4)
	O33	2.06(3)
	<M-O>	2.38
*M*5O_6	O24	1.98(3)
	O24	1.98(5)
	O24	1.98(3)
	O32	2.48(3)
	O32	2.48(5)
	O32	2.48(3)
	<M-O>	2.23
V1O_4	O11	1.82(3)
	O12	1.75(4)
	O12	1.75(5)
	O12	1.75(3)
V2O_4	O21	1.82(4)
	O22	1.84(2)
	O23	1.87(3)
	O24	1.79(2)
V3O_4	O31	1.79(3)
	O32	1.73(2)
	O33	1.98(2)
	O34	1.80(4)

Table S5. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.866}Eu_{0.44}(SbO_4)_{0.1}(VO_4)_{6.9}$.

Atom	Wyck.	S.O.F.	*x*	*y*	*z*	U [Å^2]
Ca1	18b	0.90	0.1247(13)	0.2816(11)	0.1005(2)	0.002
Eu1	18b	0.10	0.1247(13)	0.2816(11)	0.1005(2)	0.002
Ca2	18b	0.96	0.5296(14)	0.4735(14)	0.0693(2)	0.002
Eu2	18b	0.04	0.5296(14)	0.4735(14)	0.0693(2)	0.002
Ca3	18b	1	0.2198(12)	0.3930(10)	0.0093(3)	0.009
Ca4	6a	0.28	0	0	-0.0107(17)	0.041
Ca5	6a	1	0.6666	0.3333	-0.0007(7)	0.009
V1	6a	0.95	0	0	-0.1006(3)	0.001
Sb1	6a	0.05	0	0	-0.1006(3)	0.001
V2	18b		0.3502(13)	0.1964(12)	0.1345(3)	0.002
V3	18b	0.98	0.3215(9)	0.1733(14)	0.0320(3)	0.002
Sb3	18b	0.01	0.3215(9)	0.1733(14)	0.0320(3)	0.002
O11	6a	1	0	0	-0.1469(3)	0.017
O12	18b	1	0.1840(30)	0.5190(30)	0.0821(12)	0.004
O21	18b	1	0.4340(30)	0.1110(30)	0.1147(9)	0.001
O22	18b	1	0.3650(30)	0.1940(30)	0.1805(3)	0.001
O23	18b	1	0.4030(40)	0.3710(18)	0.1207(9)	0.001
O24	18b	1	0.1665(17)	0.0760(40)	0.1301(8)	0.005
O31	18b	1	0.2180(30)	-0.0101(16)	0.0409(9)	0.005
O32	18b	1	0.4955(15)	0.2440(50)	0.0486(7)	0.008
O33	18b	1	0.2660(30)	0.4450(30)	0.1453(10)	0.027
O34	18b	1	0.2600(40)	0.2740(30)	0.0545(8)	0.001

Table S6. Selected distances (Å) in $Ca_{9.866}Eu_{0.44}(SbO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O$_8$	O12	2.42(4)
	O21	2.86(4)
	O23	2.78(4)
	O24	2.73(5)
	O24	2.41(3)
	O31	2.51(3)
	O33	2.38(3)
	O34	2.31(4)
	<M-O>	2.55
*M*2O$_8$	O12	2.43(5)
	O21	2.22(4)
	O22	2.27(2)

	O23	2.33(3)
	O31	3.24(3)
	O32	2.45(3)
	O32	2.36(6)
	O34	2.69(3)
	<M-O>	2.50
$M3O_9$	O11	2.61(1)
	O12	3.20(5)
	O21	2.61(4)
	O22	2.60(4)
	O22	2.84(5)
	O23	2.58(4)
	O31	2.40(2)
	O33	3.11(3)
	O34	2.32(4)
	<M-O>	2.70
$M4O_6$	O12	3.24(7)
	O12	3.24(7)
	O12	3.24(7)
	O33	2.17(3)
	O33	2.17(3)
	O33	2.17(5)
	<M-O>	2.71
$M5O_6$	O24	2.08(3)
	O24	2.08(5)
	O24	2.08(3)
	O32	2.47(3)
	O32	2.47(5)
	O32	2.47(3)
	<M-O>	2.28
$V1O_4$	O11	1.76(2)
	O12	1.73(3)
	O12	1.73(4)
	O12	1.73(4)
$V2O_4$	O21	1.76(4)
	O22	1.76(2)
	O23	1.76(3)
	O24	1.76(2)
$V3O_4$	O31	1.76(2)
	O32	1.76(2)
	O33	2.32(4)
	O34	1.76(5)

Table S7. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.709}Eu_{0.494}(MoO_4)_{0.1}(VO_4)_{6.9}$.

Atom	**Wyck.**	**S.O.F.**	***x***	***y***	***z***	**U [Å^2]**
Ca1	18b	0.91	0.1203(11)	0.2824(9)	0.1019(2)	0.002(3)
Eu1	18b	0.09	0.1203(11)	0.2824(9)	0.1019(2)	0.002(3)
Ca2	18b	0.92	0.5293(12)	0.4700(12)	0.0719(2)	0.013(3)
Eu2	18b	0.08	0.5293(12)	0.4700(12)	0.0719(2)	0.013(3)
Ca3	18b	1	0.2079(13)	0.4006(9)	0.0118(2)	0.026(3)
Ca4	6a	0.20	0	0	-0.0188(19)	0.005
Ca5	6a	1	0.6666	0.3333	-0.0013(5)	0.007
V1	6a	0.95	0	0	-0.0988(3)	0.011
Mo1	6a	0.05	0	0	-0.0988(3)	0.011
V2	18b	1	0.3417(10)	0.1884(11)	0.1353(3)	0.014
V3	18b	0.98	0.3114(7)	0.1724(11)	0.0335(2)	0.0051
Mo3	18b	0.02	0.3114(7)	0.1724(11)	0.0335(2)	0.005
O11	6a	1	0	0	-0.1471(6)	0.002
O12	18b	1	0.1920(30)	0.5270(20)	0.0860(9)	0.012
O21	18b	1	0.4330(30)	0.1110(30)	0.1132(7)	0.006
O22	18b	1	0.3640(20)	0.1950(30)	0.1816(5)	0.004
O23	18b	1	0.4010(30)	0.3770(20)	0.1241(8)	0.001
O24	18b	1	0.1646(18)	0.0790(40)	0.1178(6)	0.0001
O31	18b	1	0.2120(30)	-0.0150(20)	0.0428(8)	0.022
O32	18b	1	0.4977(18)	0.2490(40)	0.0437(6)	0.002
O33	18b	1	0.2880(30)	0.1890(20)	-0.0110(5)	0.003
O34	18b	1	0.2400(30)	0.2730(30)	0.0523(8)	0.006

Table S8. Selected distances (Å) in $Ca_{9.709}Eu_{0.494}(MoO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O$_8$	O12	2.45(3)
	O21	2.79(4)
	O23	2.82(3)
	O24	2.56(4)
	O24	2.23(3)
	O31	2.46(3)
	O33	2.32(4)
	O34	2.25(2)
	<M-O>	2.49
*M*2O$_8$	O12	2.53(4)
	O21	2.12(3)
	O22	2.33(3)
	O23	2.34(3)
	O31	3.32(3)
	O32	2.49(4)

	O32	2.50(5)
	O34	2.88(3)
	<M-O>	2.56
*M*3O$_9$	O11	2.52(1)
	O12	3.18(3)
	O21	2.81(3)
	O22	2.73(4)
	O22	2.66(5)
	O23	2.47(3)
	O31	2.32(3)
	O33	2.96(3)
	O34	2.21(4)
	<M-O>	2.65
*M*4O$_6$	O12	2.81(7)
	O12	2.81(7)
	O12	2.81(7)
	O33	2.77(2)
	O33	2.77(4)
	O33	2.77(3)
	<M-O>	2.79
*M*5O$_6$	O24	2.38(3)
	O24	2.38(4)
	O24	2.38(3)
	O32	2.34(2)
	O32	2.34(4)
	O32	2.34(2)
	<M-O>	2.36
V1O$_4$	O11	1.84(2)
	O12	1.67(2)
	O12	1.67(3)
	O12	1.67(3)
V2O$_4$	O21	1.80(4)
	O22	1.78(2)
	O23	1.87(3)
	O24	1.81(2)
V3O$_4$	O31	1.80(2)
	O32	1.80(2)
	O33	1.74(2)
	O34	1.78(4)

Table S9. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.764}Eu_{0.457}(SO_4)_{0.1}(VO_4)_{6.9}$.

Atom	**Wyck.**	**S.O.F.**	***x***	***y***	***z***	**U [Å^2]**

Ca1	18b	0.92	0.1225(9)	0.2807(7)	0.1011(2)	0.003
Eu1	18b	0.08	0.1225(9)	0.2807(7)	0.1011(2)	0.003
Ca2	18b	0.93	0.5315(11)	0.4681(10)	0.0709(2)	0.011
Eu2	18b	0.07	0.5315(11)	0.4681(10)	0.0709(2)	0.011
Ca3	18b	1	0.2091(10)	0.3982(6)	0.0111(2)	0.014
Ca4	6a	0.22	0	0	-0.0197(16)	0.005
Ca5	6a	1	0.6666	0.3333	0.0019(4)	0.007
V1	6a	1	0	0	-0.0979(3)	0.011
V2	18b	0.97	0.3471(8)	0.1918(9)	0.1366(2)	0.014
S2	18b	0.03	0.3471(8)	0.1918(9)	0.1366(2)	0.014
V3	18b	1	0.3130(6)	0.1722(8)	0.0347(2)	0.0051
O11	6a	1	0	0	-0.1497(9)	0.0022
O12	18b	1	0.1903(19)	0.5221(18)	0.0818(8)	0.012
O21	18b	1	0.4450(30)	0.1160(20)	0.1145(6)	0.006
O22	18b	1	0.3510(16)	0.1910(20)	0.1799(5)	0.004
O23	18b	1	0.3980(30)	0.3740(20)	0.1228(7)	0.001
O24	18b	1	0.1596(19)	0.0920(30)	0.1192(6)	0.001
O31	18b	1	0.2220(30)	-0.0050(30)	0.0427(6)	0.022
O32	18b	1	0.4895(18)	0.2470(30)	0.0400(5)	0.002
O33	18b	1	0.1560(20)	0.4141(19)	0.1546(6)	0.006
O34	18b	1	0.2650(30)	0.2840(30)	0.0541(6)	0.006

Table S10. Selected distances (Å) in $Ca_{9.764}Eu_{0.457}(SO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O$_8$	O12	2.45(2)
	O21	2.93(4)
	O23	2.76(3)
	O24	2.37(3)
	O24	2.42(2)
	O31	2.48(2)
	O33	2.42(2)
	O34	2.35(3)
	<M-O>	2.52
*M*2O$_8$	O12	2.55(3)
	O21	2.12(3)
	O22	2.33(2)
	O23	2.36(3)
	O31	3.24(3)
	O32	2.50(3)
	O32	2.54(4)
	O34	2.64(3)

	<M-O>	2.54
*M*3O$_9$	O11	2.53(1)
	O12	3.06(3)
	O21	2.70(3)
	O22	2.81(4)
	O22	2.74(3)
	O23	2.52(3)
	O31	2.38(3)
	O33	2.80(3)
	O34	2.31(3)
	<M-O>	2.65
*M*4O$_6$	O12	2.93(6)
	O12	2.93(6)
	O12	2.93(6)
	O33	2.45(2)
	O33	2.45(2)
	O33	2.45(3)
	<M-O>	2.69
*M*5O$_6$	O24	2.41(2)
	O24	2.41(3)
	O24	2.41(2)
	O32	2.21(2)
	O32	2.21(4)
	O32	2.21(2)
	<M-O>	2.31
V1O$_4$	O11	1.97(4)
	O12	1.64(2)
	O12	1.64(2)
	O12	1.64(3)
V2O$_4$	O21	1.84(3)
	O22	1.65(2)
	O23	1.85(3)
	O24	1.88(2)
V3O$_4$	O31	1.69(3)
	O32	1.68(2)
	O33	1.91(2)
	O34	1.71(4)

Table S11. Atomic coordinates, displacement parameters (Å^2) and site-occupancy factors (SOFs) in the structure of $Ca_{9.825}Eu_{0.45}(AsO_4)_{0.1}(VO_4)_{6.9}$.

Atom	**Wyck.**	**S.O.F.**	***x***	***y***	***z***	**U [Å^2]**

Ca1	18b	0.88	0.1192(9)	0.2819(8)	0.1003(2)	0.003
Eu1	18b	0.12	0.1192(9)	0.2819(8)	0.1003(2)	0.003
Ca2	18b	0.96	0.5313(11)	0.4669(11)	0.0716(2)	0.011
Eu2	18b	0.04	0.5313(11)	0.4669(11)	0.0716(2)	0.011
Ca3	18b	1	0.2135(9)	0.4024(6)	0.0099(2)	0.014
Ca4	6a	0.27	0	0	-0.0123(10)	0.005
Ca5	6a	1	0.6666	0.3333	0.0037(4)	0.007
V1	6a	0.90	0	0	-0.0974(3)	0.011
As1	6a	0.10	0	0	-0.0974(3)	0.011
V2	18b	1	0.3520(10)	0.1973(9)	0.1360(2)	0.014
V3	18b	1	0.3146(7)	0.1721(10)	0.0335(2)	0.005
O11	6a	1	0	0	-0.1418(4)	0.002
O12	18b	1	-0.1436(19)	0.0120(30)	-0.0810(6)	0.008
O21	18b	1	0.4420(20)	0.1230(20)	0.1162(7)	0.006
O22	18b	1	0.3660(20)	0.1950(30)	0.1813(5)	0.0042
O23	18b	1	0.3750(30)	0.3580(30)	0.1191(7)	0.001
O24	18b	1	0.1756(19)	0.0790(30)	0.1258(7)	0.001
O31	18b	1	0.2350(30)	-0.0010(30)	0.0410(7)	0.022
O32	18b	1	0.4826(12)	0.2600(30)	0.0411(5)	0.0022
O33	18b	1	0.2650(20)	0.1790(20)	-0.0093(7)	0.003
O34	18b	1	0.2450(30)	0.2610(30)	0.0521(6)	0.006

Table S12. Selected distances (Å) in $Ca_{9.825}Eu_{0.45}(AsO_4)_{0.1}(VO_4)_{6.9}$ samples from PXRD data

Polyhedra		Distance, Å
*M*1O$_8$	O12	2.27(4)
	O21	2.91(4)
	O23	2.57(3)
	O24	2.74(3)
	O24	2.30(2)
	O31	2.52(3)
	O33	2.46(3)
	O34	2.37(3)
	<M-O>	2.52
*M*2O$_8$	O12	2.61(4)
	O21	2.21(3)
	O22	2.35(3)
	O23	2.36(3)
	O31	3.17(3)
	O32	2.34(3)
	O32	2.70(3)
	O34	2.87(3)

	<M-O>	2.58
$M3O_9$	O11	2.55(1)
	O12	3.17(3)
	O21	2.62(3)
	O22	2.66(3)
	O22	2.70(4)
	O23	2.74(3)
	O31	2.41(3)
	O33	2.84(3)
	O34	2.36(3)
	<M-O>	2.67
$M4O_6$	O12	3.08(4)
	O12	3.08(4)
	O12	3.08(4)
	O33	2.45(2)
	O33	2.45(3)
	O33	2.45(2)
	<M-O>	2.77
$M5O_6$	O24	2.37(2)
	O24	2.37(4)
	O24	2.37(2)
	O32	2.25(2)
	O32	2.25(3)
	O32	2.25(2)
	<M-O>	2.31
$V1O_4$	O11	1.69(2)
	O12	1.74(3)
	O12	1.74(4)
	O12	1.74(2)
$V2O_4$	O21	1.72(3)
	O22	1.73(2)
	O23	1.75(3)
	O24	1.73(2)
$V3O_4$	O31	1.65(3)
	O32	1.60(1)
	O33	1.73(3)
	O34	1.65(4)

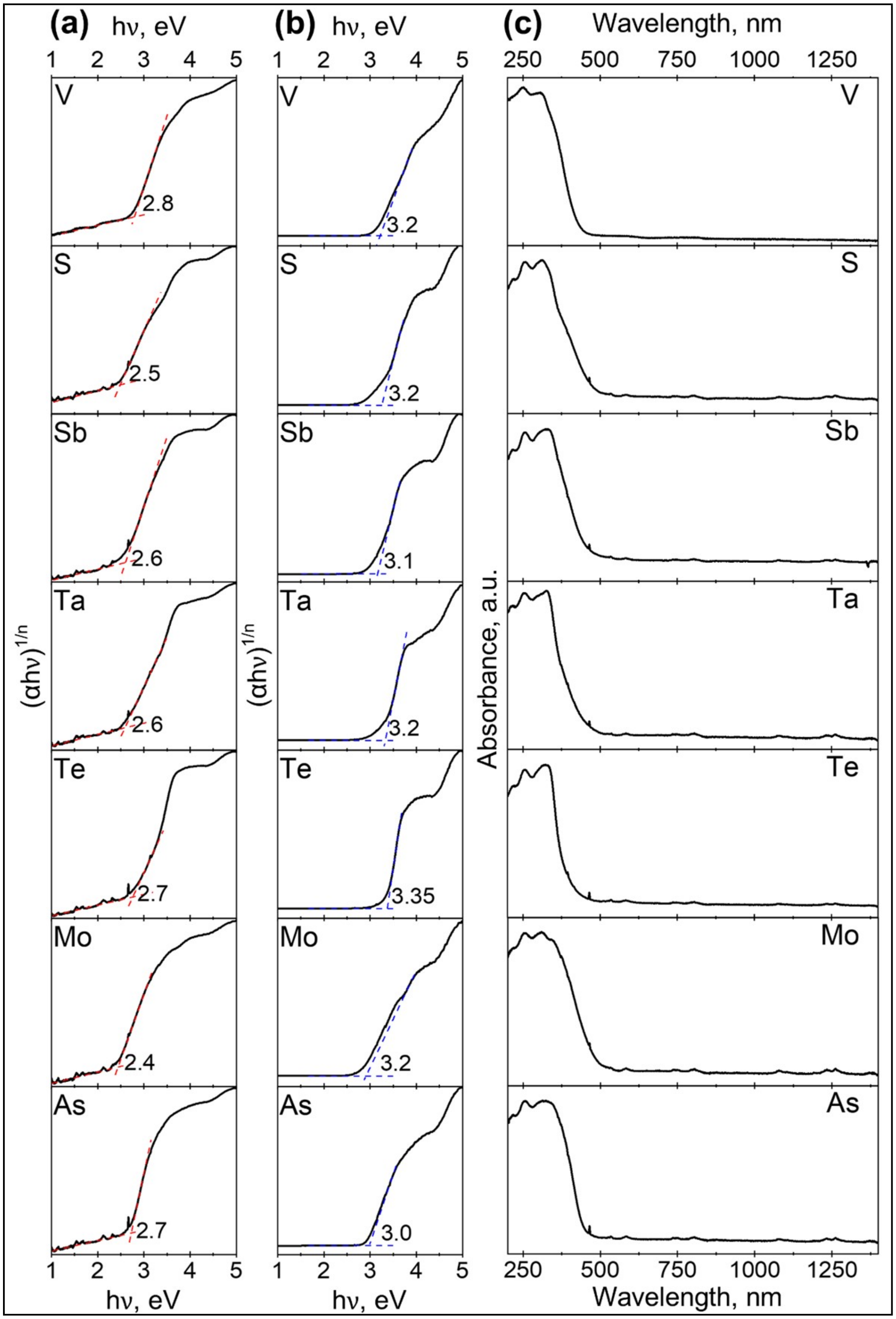


Fig. S3. Tauc plots and absorbance spectra for the $Ca_{9.75}Eu_{0.5}(VO_4)_{6.9}(XO_4)_{0.1}$ solid solutions. For each substituent X (V^{5+}, S^{6+}, Sb^{5+}, Ta^{5+}, Te^{4+}, Mo^{6+}, As^{5+}), the corresponding column shows: (a)

Tauc plot assuming a direct allowed transition (n = 2), (b) Tauc plot assuming an indirect allowed transition (n = 1/2), and (c) the absorbance spectrum ($A \sim 1 - R$). The dashed lines represent the linear extrapolations used to determine the optical band gap energies (E_g).

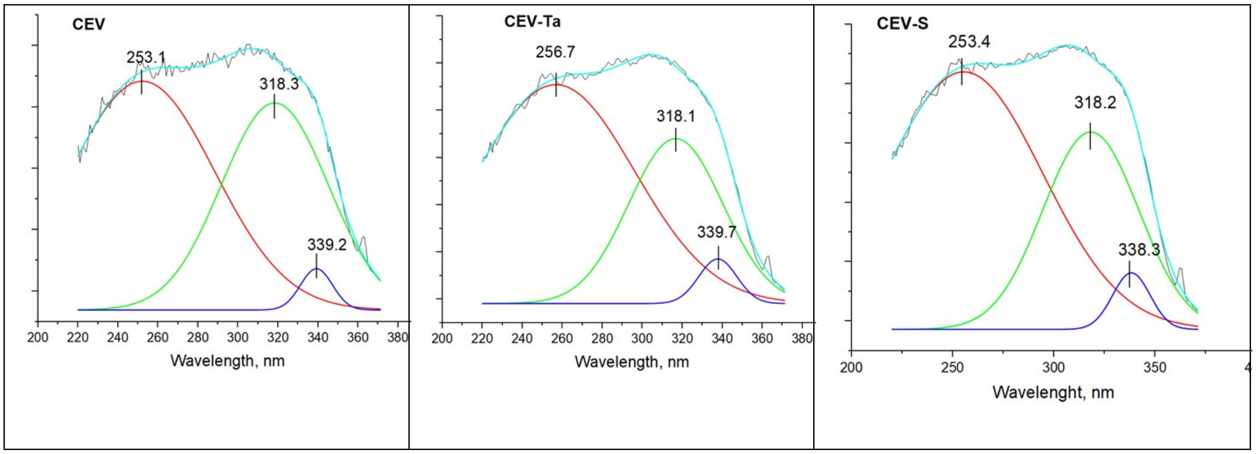
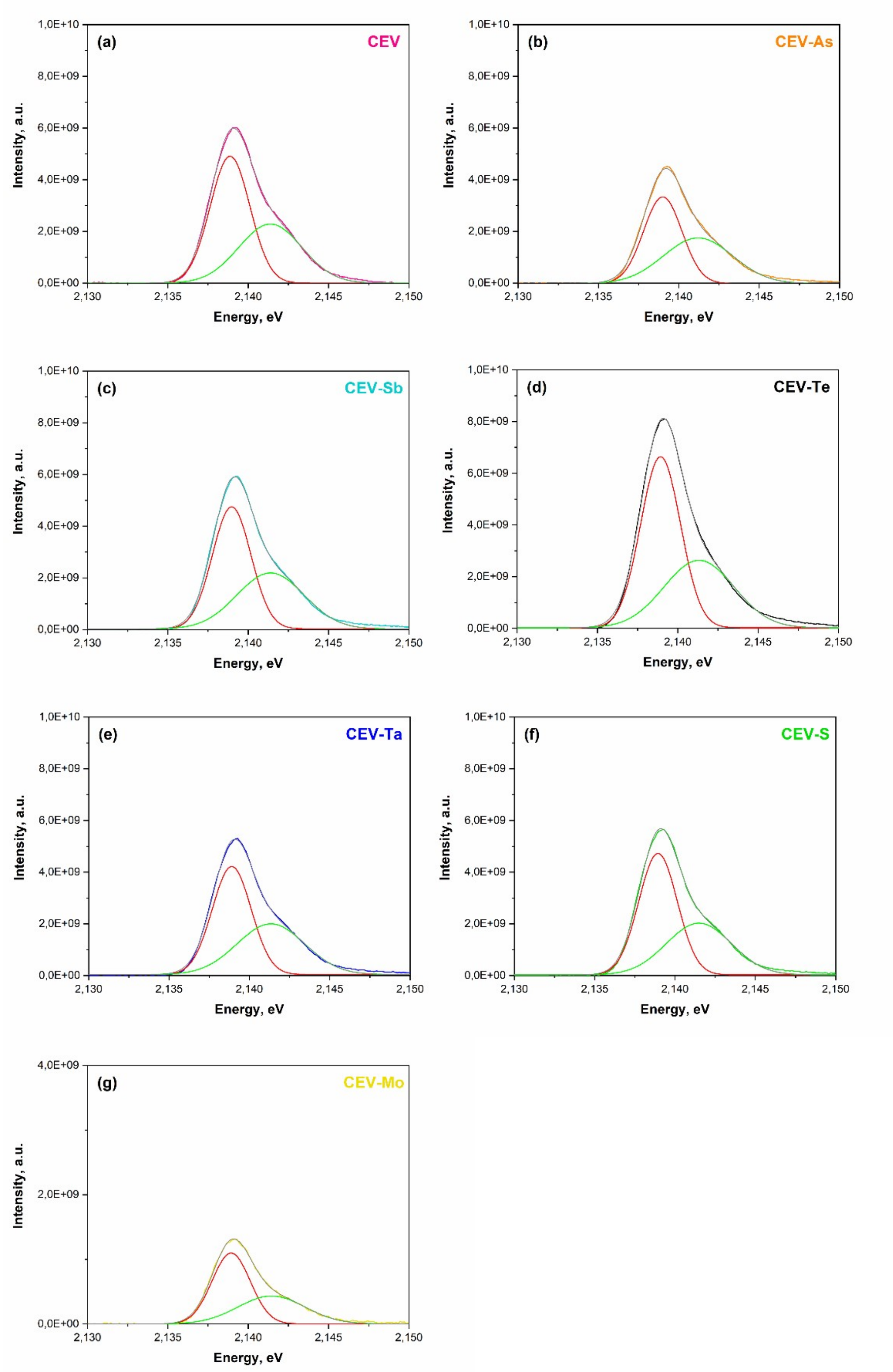


Fig. S4. Decomposition of the PLE spectra for $Ca_{9.75\pm\delta}Eu_{0.5}(XO_4)_{0.1}(VO_4)_{6.9}$ samples ($X = V^{5+}$, Ta^{5+}, S^{6+}), λ_{em} = 615 nm, T = 300 K.



(a)
CEV
(b)
CEV-As
(c)
CEV-Sb
(d)
CEV-Te
(e)
CEV-Ta
(f)
CEV-S
(g)
CEV-Mo
Intensity, a.u.
Energy, eV
1,0E+10
8,0E+09
6,0E+09
4,0E+09
2,0E+09
0,0E+00
2,130
2,135
2,140
2,145
2,150

Fig. S5. The Gaussian decomposition of the peaks at the $^5D_0 \rightarrow {}^7F_0$ transition for $Ca_{9.75\pm\delta}Eu_{0.5}(XO_4)_{0.1}(VO_4)_{6.9}$ for $X = V^{5+}$ (a), As^{5+} (b), Sb^{5+} (c), Te^{4+} (d), Ta^{5+} (e), S^{6+} (f) and Mo^{6+} (g) samples, λ_{em} = 395 nm, T = 300 K.