Electronic Supplementary Information

for

Dion-Jacobson $A'M^{III}NaNb_3O_{10}$ (A' = Rb, Cs; M(III) = Sm, Bi), $RbSmNa_2Nb_4O_{13}$ layered perovskites and their luminescent function

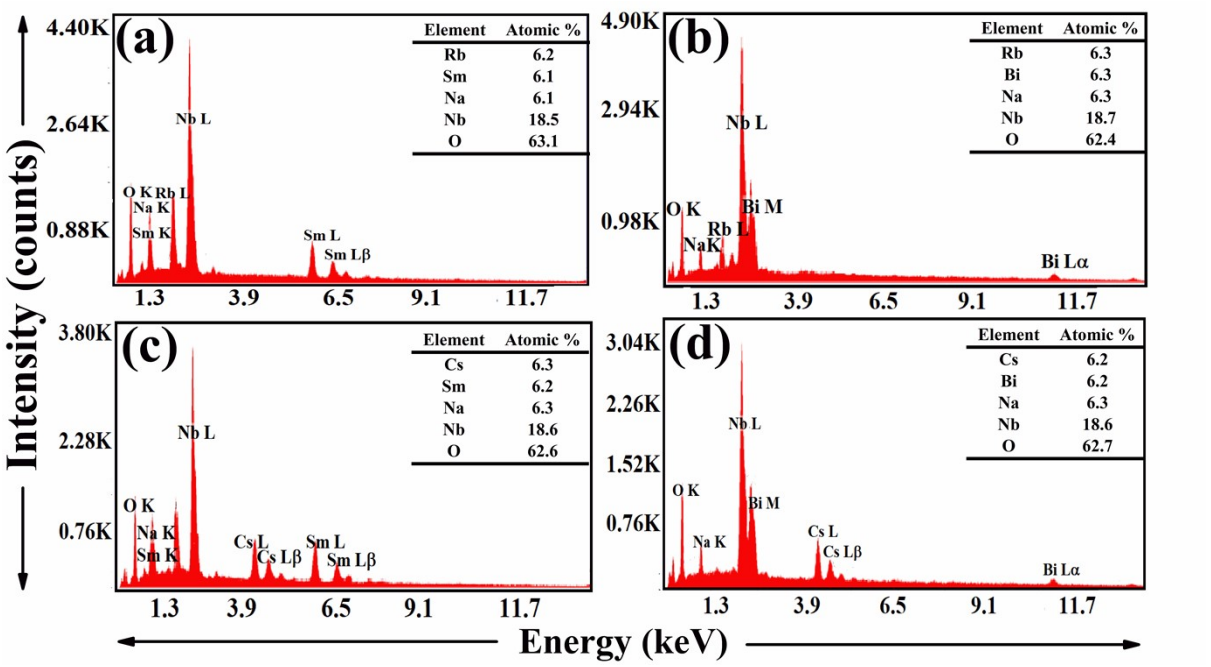

Fig. S1 EDS spectra of (a) $RbSmNaNb_3O_{10}$, (b) $RbBiNaNb_3O_{10}$, (c) $CsSmNaNb_3O_{10}$, (d) $CsBiNaNb_3O_{10}$.

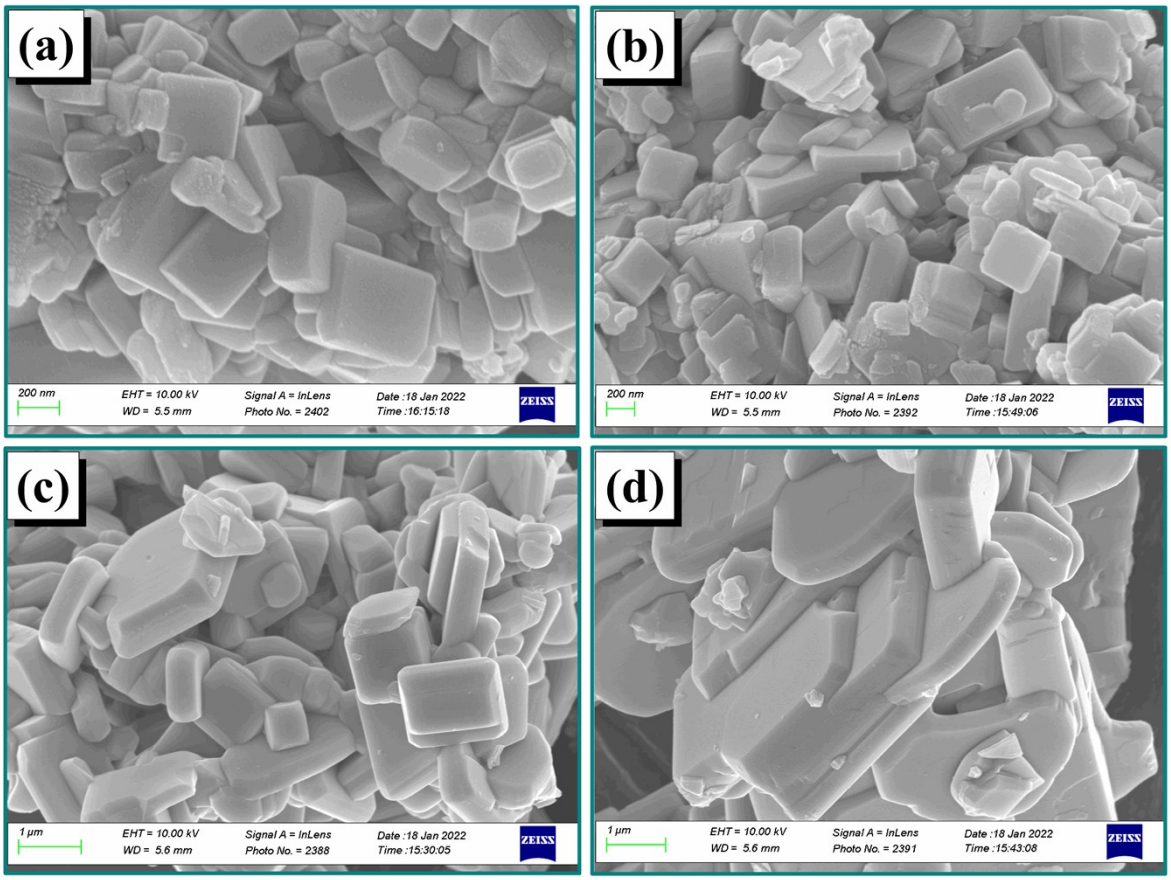

Fig. S2 FESEM images of (a) $RbSmNaNb_3O_{10}$, (b) $RbBiNaNb_3O_{10}$, (c) $CsSmNaNb_3O_{10}$, and (d) $CsBiNaNb_3O_{10}$.

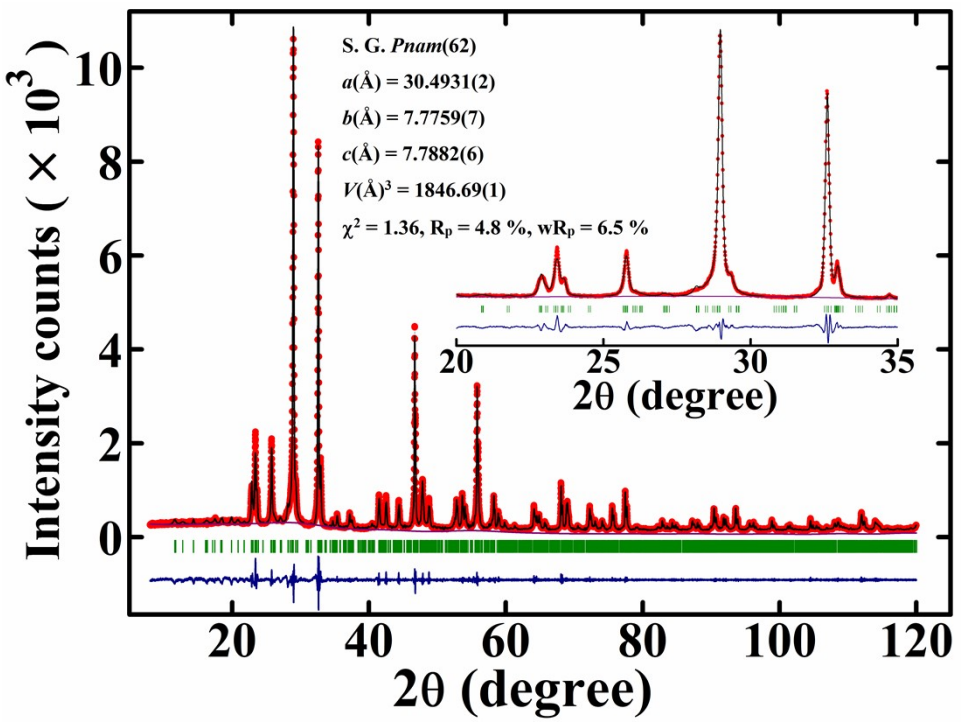

Fig. S3 Experimentally observed PXRD pattern of $CsLaNaNb_3O_{10}$ (data in red), profile matching (data in black), difference profile (data in blue), and vertical bars (data in green) indicating Bragg reflections.

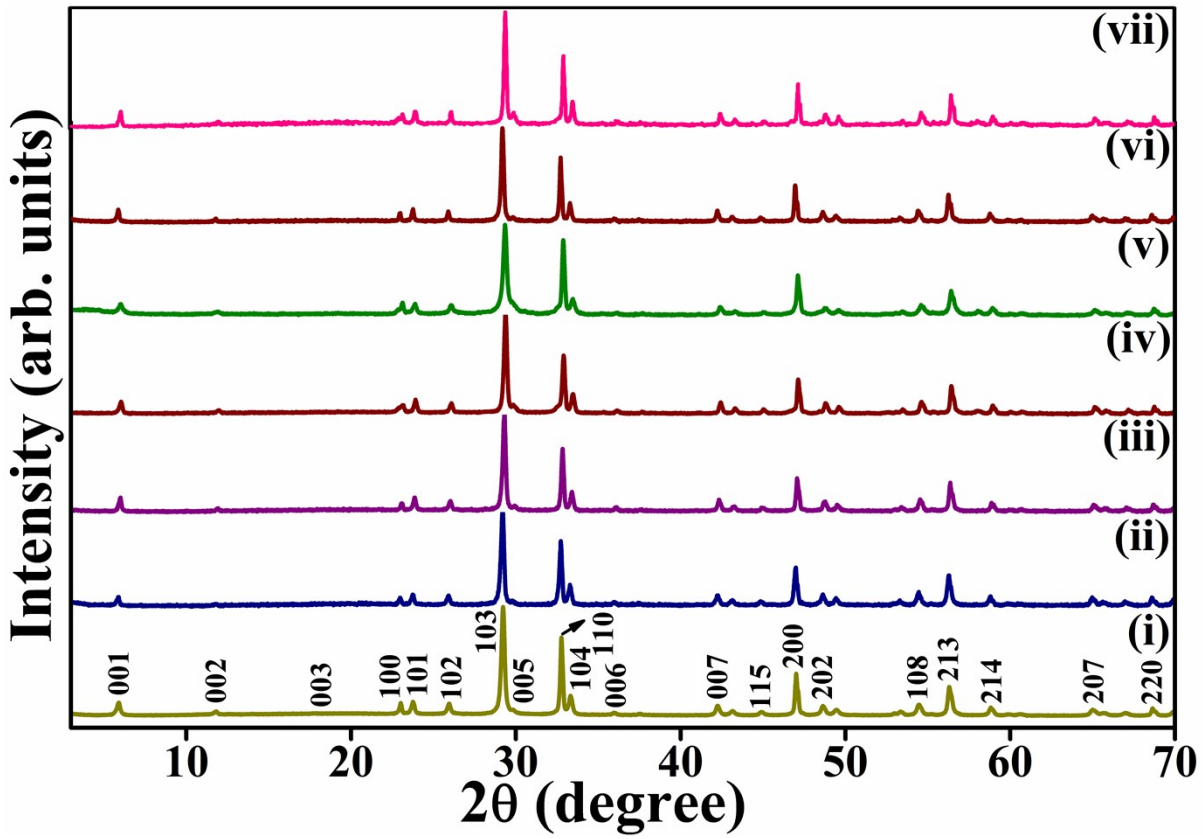

Fig. S4 PXRD patterns of $RbSmNaNb_3O_{10}$ (i), 1 (ii), 2 (iii), 5 (iv), 7 (v), 10 (vi) mol % Eu^{3+} and 5 mol % (vii) Tb^{3+}-doped samples.

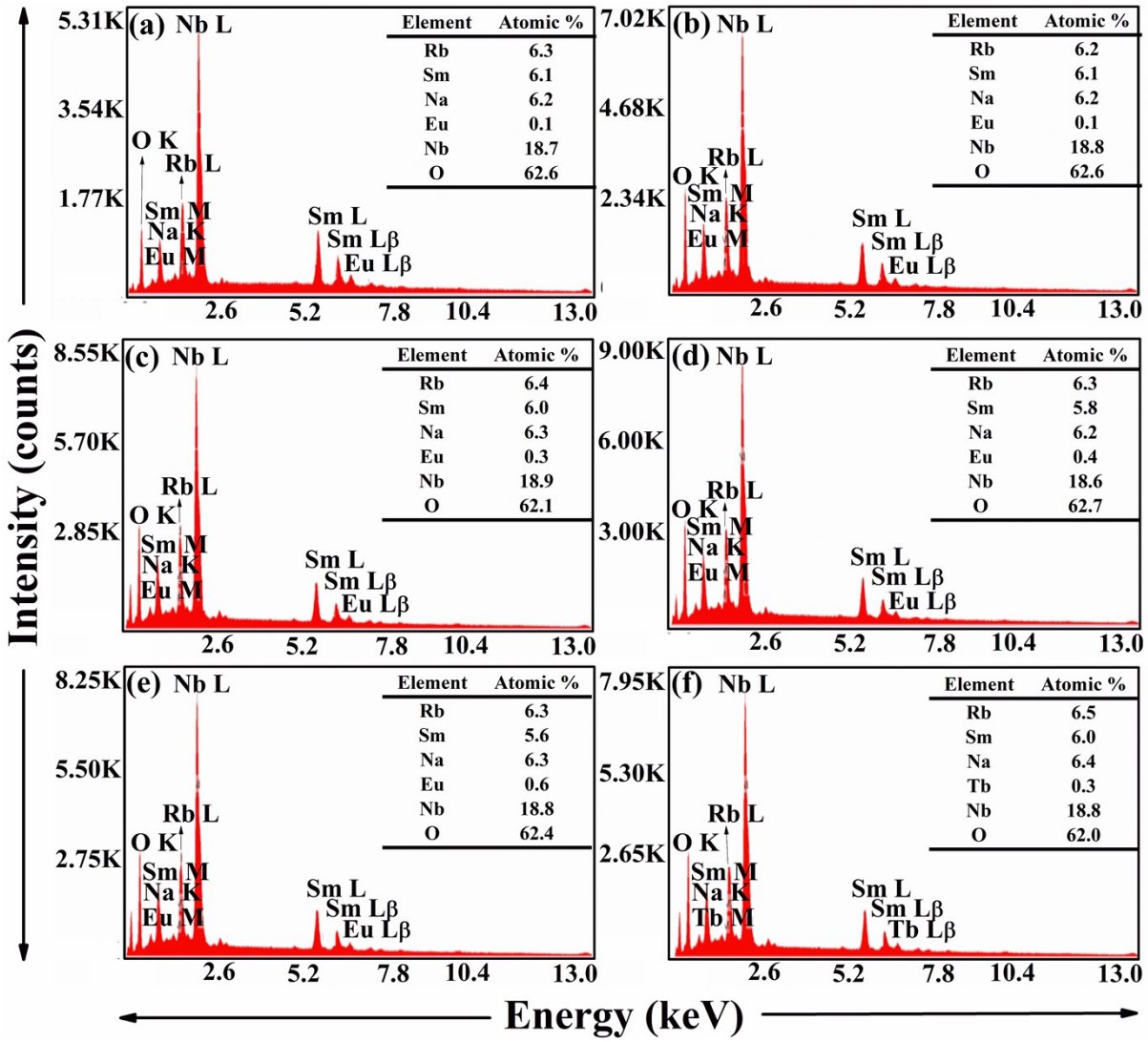

Fig. S5 EDS spectra of $RbSmNaNb_3O_{10}$ doped with (a) 1, (b) 2, (c) 5, (d) 7, (e) 10 mol % Eu^{3+} and (f) 5 mol % Tb^{3+}.

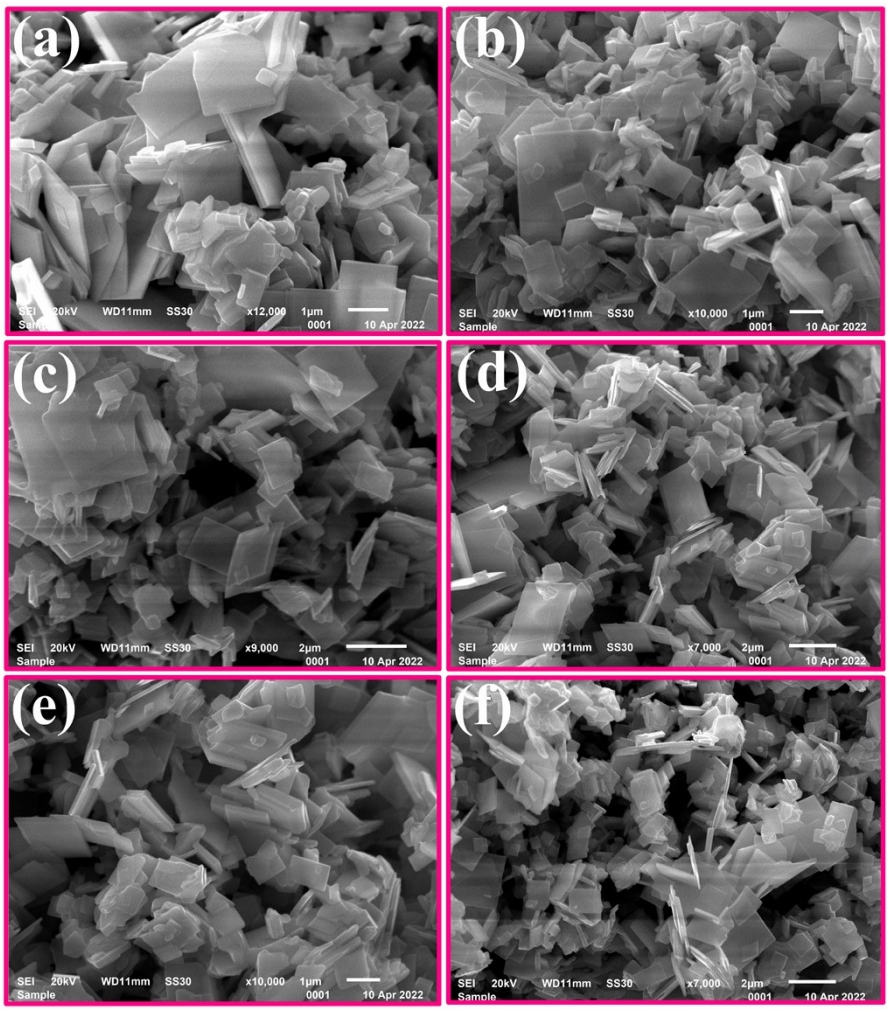

Fig. S6 SEM images of $RbSmNaNb_3O_{10}$ doped with (a) 1, (b) 2, (c) 5, (d) 7, (e) 10 mol % Eu^{3+} and (f) 5 mol % Tb^{3+}.

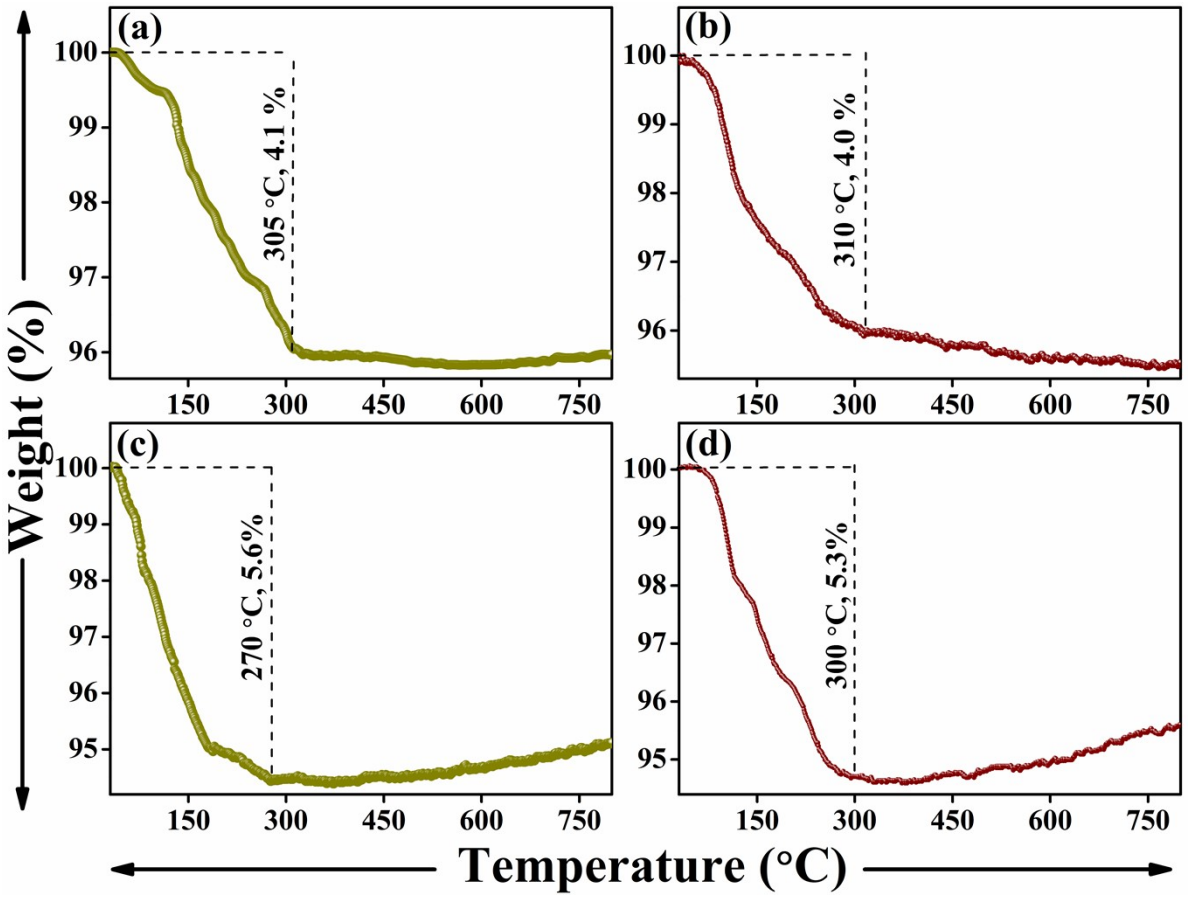

Fig. S7 TG traces of (a, b) proton and (c, d) sodium exchanged samples of parent $RbSmNaNb_3O_{10}$ and $RbBiNaNb_3O_{10}$, respectively.

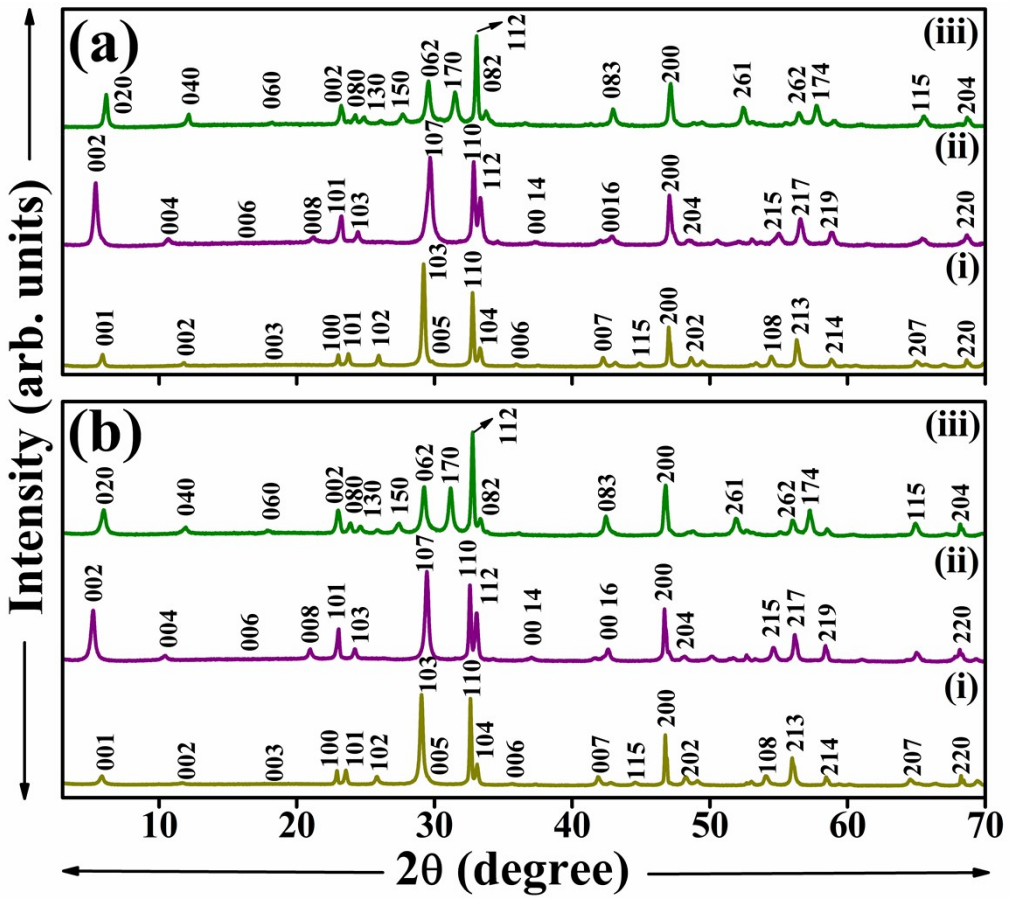

Fig. S8(a) PXRD patterns of $RbSmNaNb_3O_{10}$ (i) and the ion-exchanged products $Na(SmNa)Nb_3O_{10}\cdot 2H_2O$ (ii), $K(SmNa)Nb_3O_{10}$ (iii), and (b) PXRD patterns of $RbBiNaNb_3O_{10}$ (i) and the ion-exchanged products $Na(BiNa)Nb_3O_{10}\cdot 2H_2O$ (ii), $K(BiNa)Nb_3O_{10}$ (iii).

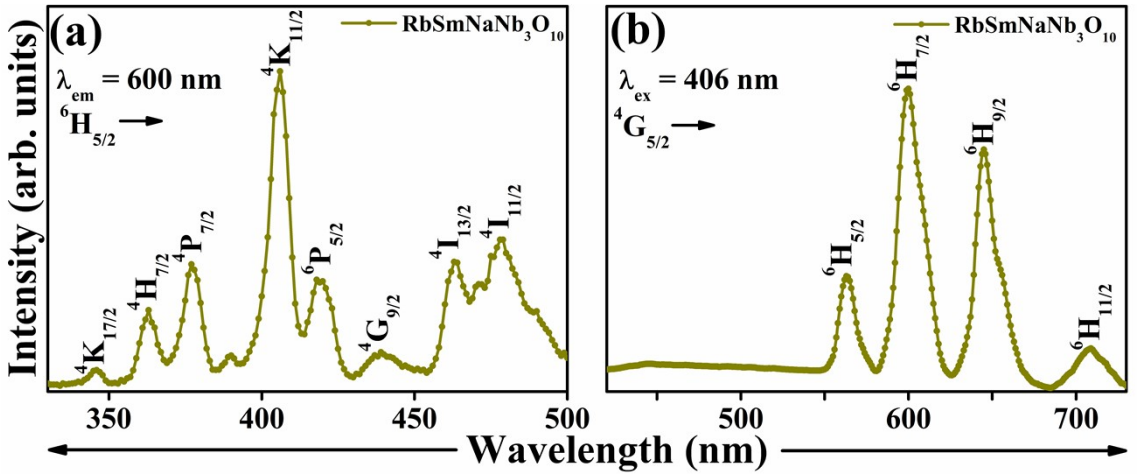

Fig. S9 (a) PL excitation and (b) emission spectra of $RbSmNaNb_3O_{10}$ sample.

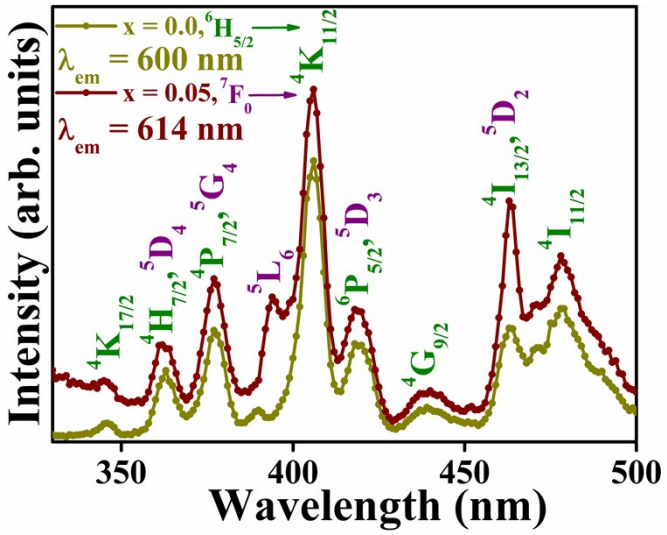

Fig. S10 Excitation spectra of $RbSmNaNb_3O_{10}$ doped with 5 mol % Eu^{3+} doped samples.

Table S1(a) Positional, occupancies and thermal parameters of $CsSmNaNb_3O_{10}$ and $CsBiNaNb_3O_{10}$.

Atoms	*Wyckoff position*	*x/a*	*y/b*	*z/c*	SOF	U(iso)Å²
Cs1	4*c*	0.2574(1)	0.2624(9)	0.25	1	0.0251(14)
Cs2	4*c*	0.2465(2)	0.7498(1)	0.25	1	0.0254(17)
Sm/Na1	4*c*	0.0720(4)	0.2722(2)	0.25	0.5	0.0243(28)
Sm/Na2	4*c*	0.0722(3)	0.7605(2)	0.25	0.5	0.0247(26)
Sm/Na3	4*c*	0.4253(4)	0.2468(18)	0.25	0.5	0.0247(14)
Sm/Na4	4*c*	0.4285(3)	0.7322(14)	0.25	0.5	0.0244(23)
Nb1	4*a*	0.0	0.0	0.0	1	0.0248(18)
Nb2	4*b*	0.0	0.5	0.0	1	0.0248(22)
Nb3	8*d*	0.1402(3)	0.0084(11)	0.0021(10)	1	0.0236(14)
Nb4	8*d*	0.3597(2)	0.0014(9)	0.0017(8)	1	0.0238(12)
O1	8*d*	0.1992(4)	0.516(5)	0.506(4)	1	0.015(4)
O2	8*d*	0.1983(4)	0.0236(35)	0.0185(29)	1	0.020(5)
O3	8*d*	0.4347(5)	0.476(4)	0.0507(21)	1	0.022(6)
O4	8*d*	0.0596(5)	0.5480(26)	0.0423(27)	1	0.043(8)
O5	8*d*	0.0080(7)	0.2345(6)	0.0638(20)	1	0.047(7)
O6	8*d*	0.1180(4)	0.2128(23)	0.506(4)	1	0.010(4)
O7	8*d*	0.3722(5)	0.230(4)	0.500(5)	1	0.015(4)
O8	4*c*	0.5075(2)	0.528(5)	0.25	1	0.017(9)
O9	4*c*	0.4836(9)	0.956(5)	0.25	1	0.043(13)
O10	4*c*	0.1189(5)	0.0156(6)	0.25	1	0.0235(12)
O11	4*c*	0.3799(8)	0.0115(3)	0.25	1	0.0252(10)
O12	4*c*	0.1324(6)	0.485(4)	0.25	1	0.0249(15)
O13	4*c*	0.3721(9)	0.477(7)	0.25	1	0.0255(15)
Space group: *Pnam* (62); *a* (Å) = 30.2952(2), *b* (Å) = 7.7548(5), *c* (Å) = 7.7559(6), *V* (Å^3) = 1822.14(2); Z = 8; χ^2 = 1.1, R_p = 3.9 %, R_{wp} = 5.3 %.						
Cs1	4*c*	0.2570(2)	0.2574(18)	0.25	1	0.0288(18)
Cs2	4*c*	0.2470(1)	0.7499(21)	0.25	1	0.0300(17)
Bi/Na1	4*c*	0.0726(3)	0.2659(21)	0.25	0.5	0.0319(23)
Bi/Na2	4*c*	0.0730(2)	0.7579(21)	0.25	0.5	0.0366(20)
Bi/Na3	4*c*	0.4256(2)	0.2422(21)	0.25	0.5	0.0291(21)
Bi/Na4	4*c*	0.4277(2)	0.7274(23)	0.25	0.5	0.0357(21)
Nb1	4*b*	0.0	0.5	0.0	1	0.0138(23)
Nb2	8*d*	0.1415(7)	0.0072(10)	0.0016(7)	1	0.0222(19)
Nb3	8*d*	0.3595(7)	0.0007(9)	0.0018(7)	1	0.0197(19)
Nb4	4*a*	0.0	0.0	0.0	1	0.0286(29)
O1	8*d*	0.2021(4)	0.491(6)	0.509(5)	1	0.026(10)
O2	8*d*	0.1978(4)	0.042(4)	0.021(4)	1	0.027(12)
O3	8*d*	0.4321(5)	0.4571(34)	0.0395(32)	1	0.051(10)
O4	8*d*	0.0552(4)	0.543(4)	0.026(4)	1	0.025(9)
O5	8*d*	0.0045(10)	0.2355(7)	0.0600(26)	1	0.014(6)
O6	8*d*	0.1208(5)	0.243(7)	0.520(6)	1	0.0249(11)
O7	8*d*	0.3650(5)	0.25065(31)	0.512(6)	1	0.031(7)
O8	4*c*	0.5049(12)	0.552(7)	0.25	1	0.010(8)
O9	4*c*	0.4960(13)	0.552(7)	0.25	1	0.047(13)
O10	4*c*	0.1220(8)	0.0086(7)	0.25	1	0.012(13)
O11	4*c*	0.3769(8)	0.002(7)	0.25	1	0.0244(13)
O12	4*c*	0.1306(8)	0.489(7)	0.25	1	0.039(17)
O13	4*c*	0.3557(9)	0.507(7)	0.25	1	0.051(15)
Space group: *Pnam* (62); *a* (Å) = 30.5260(9), *b* (Å) = 7.7990(2), *c* (Å) = 7.8058(2), *V* (Å^3) = 1858.36(16); Z = 8; χ^2 = 1.2, R_p = 6.7 %, R_{wp} = 8.7 %.						

Table S1(b) Selected bond distances, theoretical and calculated BVS for $CsSmNaNb_3O_{10}$.

Atoms	Interatomic distances (Å)	Theoretical BVS	Calculated BVS
Cs1-O1	2.997(5) × 2	1.0	1.13
Cs1-O1	3.299(4) × 2		
Cs1-O2	3.127(5) × 2		
Cs1-O2	3.210(5) × 2		
Cs2-O1	3.042(6) × 2	1.0	1.11
Cs2-O1	3.253(6) × 2		
Cs2-O2	3.148(6) × 2		
Cs2-O2	3.188(5) × 2		
Sm/Na1-O4	2.723(10) × 2	2.0	2.03
Sm/Na1-O5	2.434(18) × 2		
Sm/Na1-O6	2.473(7) × 2		
Sm/Na1-O8	3.023(12) × 1		
Sm/Na1-O9	3.422(12) × 1		
Sm/Na1-O10	2.425(12) × 1		
Sm/Na1-O12	2.480(12) × 1		
Sm/Na1-O3	3.264(8) × 2		
Sm/Na2-O4	2.393(9) × 2	2.0	1.97
Sm/Na2-O5	3.442(7) × 2		
Sm/Na2-O7	2.582(7) × 2		
Sm/Na2-O8	2.508(11) × 1		
Sm/Na2-O9	3.212(10) × 1		
Sm/Na2-O10	2.366(12) × 1		
Sm/Na2-O12	2.867(11) × 1		
Sm/Na2-O3	2.830(7) × 2		
Sm/Na3-O13	2.361(12) × 1	2.0	2.22
Sm/Na3-O4	2.808(8) × 2		
Sm/Na3-O5	2.912(12) × 2		
Sm/Na3-O7	2.512(7) × 2		
Sm/Na3-O8	3.300(12) × 1		
Sm/Na3-O9	2.912(12) × 1		
Sm/Na3-O11	2.307(12) × 1		
Sm/Na3-O3	2.341(9) × 2		
Sm/Na4-O13	2.657(10) × 1	2.0	2.04
Sm/Na4-O4	1.871(10) × 2		
Sm/Na4-O5	3.090(11) × 2		
Sm/Na4-O6	2.363(6) × 2		
Sm/Na4-O8	2.876(10) × 1		
Sm/Na4-O9	2.366(10) × 1		
Sm/Na4-O11	2.596(11) × 1		
Sm/Na4-O3	2.558(9) × 2		

Nb1-O4	1.871(10) × 2	5.0	4.78
Nb1-O5	2.131(6) × 2		
Nb1-O9	2.030(10) × 2		
Nb2-O2	1.779(7) × 1	5.0	5.12
Nb2-O13	1.998(7) × 1		
Nb2-O6	1.800(8) × 1		
Nb2-O7	2.181(8) × 1		
Nb2-O10	2.031(7) × 1		
Nb2-O3	2.309(7) × 1		
Nb3-O1	1.775(7) × 1	5.0	4.85
Nb3-O4	2.514(7) × 1		
Nb3-O6	2.243(7) × 1		
Nb3-O7	1.836(7) × 1		
Nb3-O11	2.027(6) × 1		
Nb3-O12	1.973(6) × 1		
Nb4-O5	1.900(6) × 2	5.0	5.25
Nb4-O8	1.964(10) × 2		
Nb4-O3	2.026(12) × 2		

Table S1(c) Selected bond distances, theoretical and calculated BVS for $CsBiNaNb_3O_{10}$.

Atoms	Interatomic distances (Å)	Theoretical BVS	Calculated BVS
Cs1-O1	3.185(4) × 2	1.0	1.05
Cs1-O1	3.122(6) × 2		
Cs1-O2	3.068(5) × 2		
Cs1-O2	3.348(5) × 2		
Cs2-O1	3.021(5) × 2	1.0	1.06
Cs2-O1	3.263(5) × 2		
Cs2-O2	3.209(6) × 2		
Cs2-O2	3.211(5) × 2		
Bi/Na1-O4	2.741(3) × 2	2.0	1.79
Bi/Na1-O5	2.576(7) × 2		
Bi/Na1-O6	2.547(5) × 2		
Bi/Na1-O8	3.283(6) × 1		
Bi/Na1-O9	3.248(6) × 1		
Bi/Na1-O10	2.498(4) × 1		
Bi/Na1-O12	2.494(3) × 1		
Bi/Na1-O3	3.246(5) × 2		
Bi/Na2-O4	2.391(6) × 2	2.0	1.89
Bi/Na2-O5	3.379(4) × 2		
Bi/Na2-O7	2.696(5) × 2		
Bi/Na2-O8	2.621(6) × 1		
Bi/Na2-O9	2.847(6) × 1		
Bi/Na2-O10	2.451(4) × 1		
Bi/Na2-O12	2.767(3) × 1		
Bi/Na2-O3	2.755(5) × 2		
Bi/Na3-O13	2.872(3) × 1	2.0	1.89
Bi/Na3-O4	2.799(5) × 2		
Bi/Na3-O5	2.768(6) × 2		
Bi/Na3-O7	2.721(5) × 2		
Bi/Na3-O8	3.362(5) × 1		
Bi/Na3-O9	3.147(6) × 1		
Bi/Na3-O11	2.293(4) × 1		
Bi/Na3-O3	2.425(2) × 2		
Bi/Na4-O13	2.705(2) × 1	2.0	1.74
Bi/Na4-O4	3.369(6) × 2		
Bi/Na4-O5	3.248(3) × 2		
Bi/Na4-O6	2.413(4) × 2		
Bi/Na4-O8	2.652(5) × 1		
Bi/Na4-O9	2.688(2) × 1		
Bi/Na4-O11	2.667(5) × 1		
Bi/Na4-O3	2.659(2) × 2		

Nb1-O4	1.828(5) × 2	5.0	5.20
Nb1-O5	2.120(5) × 2		
Nb1-O9	2.000(6) × 2		
Nb2-O2	1.734(5) × 1	5.0	4.93
Nb2-O13	1.963(6) × 1		
Nb2-O6	2.073(6) × 1		
Nb2-O7	2.000(7) × 1		
Nb2-O10	2.033(6) × 1		
Nb2-O3	2.356(7) × 1		
Nb3-O1	1.860(5) × 1	5.0	4.73
Nb3-O4	2.558(7) × 1		
Nb3-O6	1.959(6) × 1		
Nb3-O7	1.958(5) × 1		
Nb3-O11	2.027(6) × 1		
Nb3-O12	1.987(6) × 1		
Nb4-O5	1.900(2) × 2	5.0	5.07
Nb4-O8	1.994(6) × 2		
Nb4-O3	2.039(6) × 2		