Supplementary Information for:

The luminescence of $Na_xEu^{3+}_{2/3-x/3}MoO_4$ scheelites depends on the number of Eu-clusters occurring in their incommensurately modulated structure

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Table S1. Chemical, crystallographic data and characteristics of the structure refinements for the $Na_xEu_{2/3-x/3}MoO_4$ compounds.

Refined composition [found by ICP-OES]	Lattice constants, Å & deg.	Modulation vector $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^*$	λ , Å	R(obs); Rw(obs); R(all); Rw(all); GOF; Rp; Rwp
$Na_{0.5}Eu_{0.5}MoO_4$ [a] $[Na_{0.54(2)}Eu_{0.505(5)}Mo_{1.00(1)}]$	a = 5.2421(1), b = 5.2385(1), c = 11.4543(2); γ = 89.949(3)	None	0.6942	0.0236; 0.0314; 0.0265; 0.0328; 0.93 0.0232; 0.0343
$Na_{0.25}Eu_{0,583}MoO_4$ [b] $[Na_{0.248(5)}Eu_{0.584(6)}Mo_{1.000(2)}]$	a = 5.23935(16), b = 5.23955(17), c = 11.5155(1); γ = 90.058(2)	0.5752(2)**a*** - 1.1939(2)**b***	0.6692	0.0214; 0.0334; 0.0231; 0.0341; 1.36; 0.0284; 0.0375
$Na_{0.236}Eu_{0,588}MoO_4$ [b] $[Na_{0.240(8)}Eu_{0.587(6)}Mo_{1.00(1)}]$	a = 5.2395(1), b = 5.2382(1), c = 11.5089(2); γ = 90.042(1)	0.5721(1)**a*** - 1.1917(1)**b***	0.703	0.019; 0.0292; 0.020; 0.0295; 1.15; 0.0235; 0.0302
$Na_{0.2}Eu_{0,6}MoO_4$ [b] $[Na_{0.214(4)}Eu_{0.602(6)}Mo_{1.000(14)}]$	a = 5.2329(3), b = 5.2339(3), c = 11.5210(2); γ = 89.939(3)	0.5754(2)**a*** - 1.1945(2)**b***	0.6942	0.0315; 0.0397; 0.0342; 0.0409; 1.66; 0.0298; 0.0405
$Na_{0.138}Eu_{0,621}MoO_4$ [b] $[Na_{0.142(4)}Eu_{0.619(5)}Mo_{1.00(1)}]$	a = 5.2388(1), b = 5.2442(1), c = 11.5592(2); γ = 90.1776(5)	0.58600(5)**a*** - 1.20334(6)**b***	0.7117	0.0208; 0.0313; 0.0211; 0.0314; 1.33; 0.0234; 0.0308
$Na_{0.134}Eu_{0,622}MoO_4$ [b] $[Na_{0.091(2)}Eu_{0.636(7)}Mo_{1.000(11)}$ [c]$]$	a = 5.2318(3), b = 5.2310(3), c = 11.5331(2); γ = 90.232(2)	0.5987(2)**a*** - 1.2134(2)**b***	0.6942	0.0243; 0.0262; 0.0246; 0.0263;

				1.67; 0.0283 0.0414
$Na_{0.015}Eu_{0.662}MoO_4$ [b] [$Na_{0.091(2)}Eu_{0.636(7)}Mo_{1.000(11)}$ [c]]	a = 5.228(3), b = 5.230(3), c = 11.486(4); γ = 90.98(4)	0.6613(8)**a*** - 1.3265(11)**b***	0.6942	0.0246; 0.0297; 0.0246; 0.0297; 1.67; 0.0283 0.0414

[a] $I2_1/a$ 3D space group; [b] $I2/b(\alpha\beta0)00$ (3+1)D superspace group; [c] $Na_{0.091(2)}Eu_{0.636(7)}Mo_{1.000(11)}$ found by ICP-OES for the sample containing 94% $Na_{0.134}Eu_{0.622}MoO_4$ + 6% $Na_{0.014}Eu_{0.662}MoO_4$.

Details of the crystal structure refinements

$Na_{0.5}Eu_{0,5}MoO_4$ and $Na_{0.286}Eu_{0,571}MoO_4$ have been refined in the conventional $I2_1/a$ space group as 3D structures, while $I2/b(\alpha\beta0)00$ (3+1)D superspace group has been applied for all others incommensurately modulated structures. In both cases, four atomic positions were taken into account: *M* = (Na,Eu), Mo, O1 and O2. All structures have been refined with isotropic atomic displacements. Both O-positions were restricted with identical atomic displacement for each structure. Na and Eu were also restricted with identical atomic displacement and atomic coordinates for each structure.

For each incommensurately modulated structure:

i. The crenel function (Diagram S1) has been applied for the refinement of Na, Eu1 and Eu2 atomic domains of *M* position;
ii. Lengths of three atomic domains and their centers were refined;
iii. Only the first order harmonic has been used for the displacive modulations of each atom.

The phase with $x = 0.134$ has been refined along with 6% of another phase with $x = 0.014$. The final coordinates, isotropic displacement parameters, Fourier amplitudes of the displacive modulation function and characteristics of atomic domains are listed in Table S2. The Rietveld plots of calculated and different profiles are presented in Figures S1.

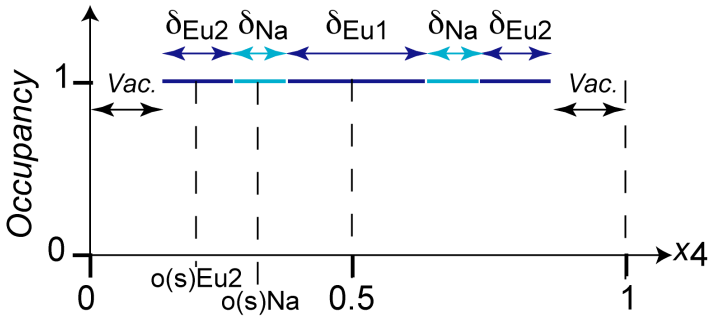

Diagram S1. Schematic representation of the occupation modulation function of the *M* position.

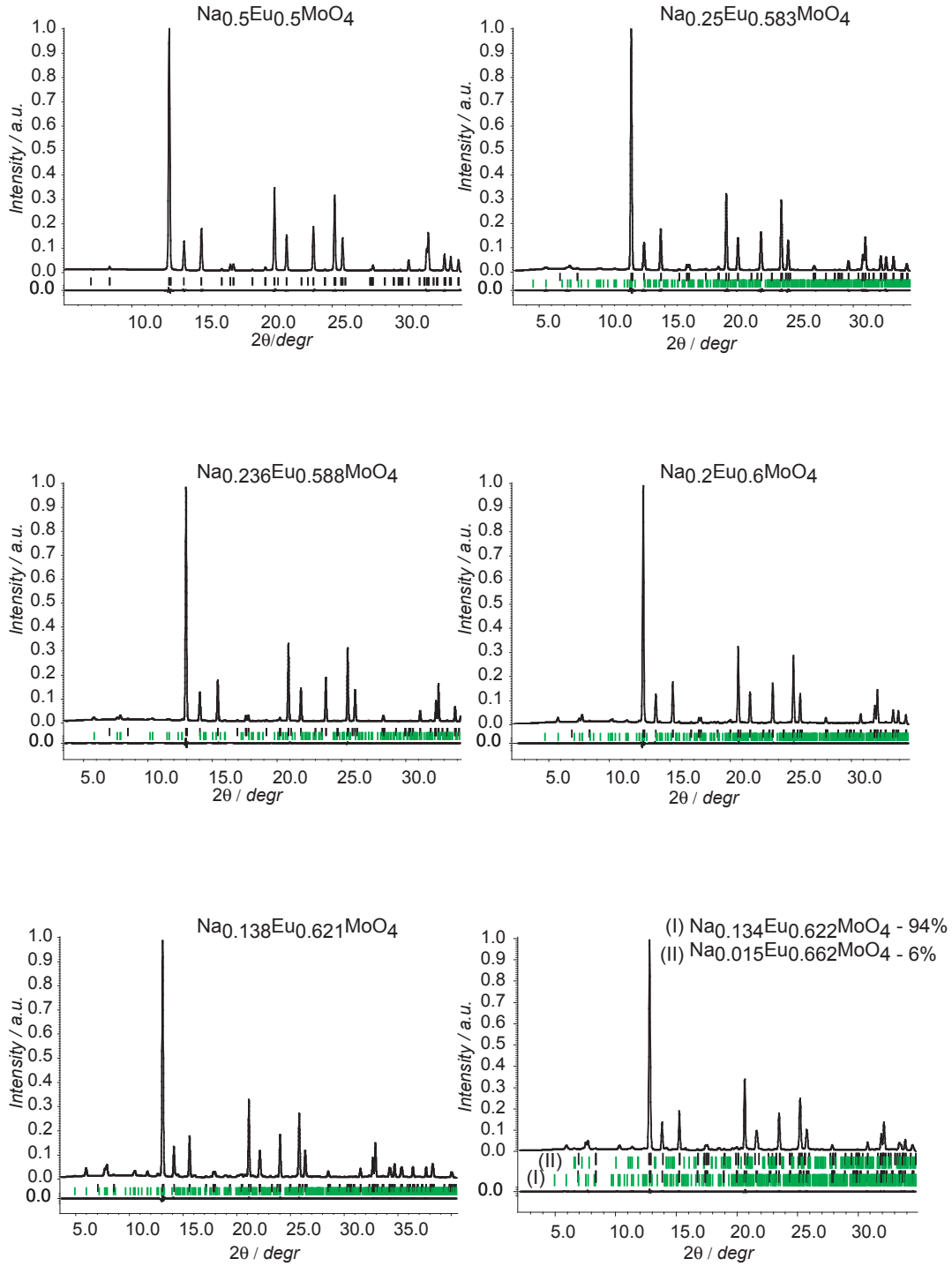

Figure S1. The Rietveld plots of calculated and residual profiles of the $Na_xEu_{3+2/3-x/3}MoO_4$ compounds. The black and green strips indicate positions of main and satellite reflections, respectively.

Table S2. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function for $Na_xEu_{2/3-x/3}MoO_4$. The waves are sorted by the terms *s* for sinus, *c* for cosines and order *n*.

Atom	Occupation; parameters of atomic domains*	Wave	*x*	*y*	*z*	U_{eq} (Å^2)
$Na_{0.5}Eu_{0.5}MoO_4$; *I*2$_1$/*a* space group						
M	1($Na_{0.5}Eu_{0.5}$)	-	0.5	0.25	0.8758(4)	0.0077(5)
Mo	1 Mo	-	0.5	0.25	0.3738(4)	0.0097(5)
O1	1 O	_	0.3731(10)	0.0159(16)	0.2810(7)	0.0017(8)
O2	1 O	_	0.7493(19)	0.4340(12)	0.0478(6)	0.0017(8)
$Na_{0.25}Eu_{0.583}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group						
M	0.5834Eu + 0.2496Na =δ_{Eu1} + 2δ_{Eu2} + 2δ_{Na};		0.5	0.25	0.8723(2)	0.0091(2)
	δ_{Eu1} = 0.3208(3), o(s)Eu1 = 0.5;					
	δ_{Na} = 0.1249(4), o(s)Na = 0.27714(7);					
	δ_{Eu2} = 0.1313(1), o(s)Eu2 = 0.1491(3)					
		s,1	-0.0029(4)	-0.0006(3)	0	
		c,1	0	0	-0.0036(3)	
Mo	1 Mo		0.5	0.25	0.3752(2)	0.0122(7)
		s,1	0.0051(5)	0.0076(4)	0	
		c,1	0	0	-0.0043(3)	
O1	1 O		0.3263(7)	0.0004(8)	0.3013(3)	0.0037(11)
		s,1	0.002(2)	-0.001(2)	0.0000(9)	
		c,1	-0.007(2)	-0.017(2)	-0.0005(8)	
O2	1 O		0.7652(8)	0.3801(6)	0.0288(4)	0.0037(11)
		s,1	-0.014(2)	0.005(2)	0.0017(8)	
		c,1	0.003(2)	0.0165(14)	0.0133(9)	
$Na_{0.236}Eu_{0.588}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group						
M	0.58818Eu + 0.2354Na =δ_{Eu1} + 2δ_{Eu2} + δ_{Na}		0.5	0.25	0.8734(2)	0.0082(5)
	δ_{Eu1} = 0.3327(2), o(s)Eu1 = 0.5;					
	δ_{Na} = 0.1177(3), o(s)Na = 0.27479(6);					
	δ_{Eu2} = 0.12774(12), o(s)Eu2 = 0.1521(2)					
		s,1	-0.0065(3)	-0.0071(3)	0	

		c,1	0	0	-0.0026(3)	
Mo	1Mo		0.5	0.25	0.3760(2)	0.0106(2)
		s,1	0.0050(4)	0.0062(4)	0	
		c,1	0	0	-0.0020(3)	
O1	1 O		0.3293(8)	-0.0053(10)	0.2953(4)	0.0061(5)
		s,1	0.0076(14)	-0.0184(15)	0.0021(7)	
		c,1	-0.0024(17)	-0.0087(16)	0.0021(7)	
O2	1 O		0.7648(8)	0.3814(7)	0.0340(4)	0.0061(5)
		s,1	-0.008(2)	0.0088(17)	-0.0009(6)	
		c,1	0.0134(14)	0.0007(12)	0.0004(7)	

$Na_{0.2}Eu_{0.6}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group

M	0.6001Eu + 0.2Na = δ_{Eu1} + 2δ_{Eu2} + 2δ_{Na}; δ_{Eu1} = 0.3393(5), o(s)Eu1 = 0.5; δ_{Na} = 0.1000(8), o(s)Na = 0.28038(13); δ_{Eu2} = 0.1304(3), o(s)Eu2 = 0.1652(5)		0.5	0.25	0.8760(7)	0.0092(6)
		s,1	-0.0074(6)	-0.0026(5)	0	
		c,1	0	0	0.0012(13)	
Mo	1 Mo		0.5	0.25	0.3750(6)	0.0155(7)
		s,1	0.0100(8)	0.0077(7)	0	
		c,1	0	0	0.0007(11)	
O1	1 O		0.3711(14)	0.0188(18)	0.2782(8)	0.0047(16)
		s,1	0.004(3)	-0.002(3)	0.0004(15)	
		c,1	0.011(3)	-0.031(3)	-0.0009(12)	
O2	1 O		0.7518(18)	0.4361(15)	0.0507(6)	0.0047(16)
		s,1	-0.004(4)	-0.003(4)	-0.0048(13)	
		c,1	0.005(3)	0.018(3)	0.0037(13)	

$Na_{0.138}Eu_{0.621}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group

M	0.6206Eu + 0.138Na = δ_{Eu1} + 2δ_{Eu2} + 2δ_{Na}; δ_{Eu1} = 0.4024(15), o(s)Eu1 = 0.5; δ_{Na} = 0.069(3), o(s)Na = 0.2643(14); δ_{Eu2} = 0.1091(9), o(s)Eu2 = 0.175(3)		0.5	0.25	0.8727(3)	0.0084(2)
		s,1	-0.0080(2)	-0.0062(2)	0	
		c,1	0	0	0.0040(3)	
Mo	1 Mo		0.5	0.25	0.3746(3)	0.0109(3)

		s,1	0.0117(2)	0.0129(2)	0	
		c,1	0	0	-0.0045(2)	
O1	1 O		0.3440(7)	0.0082(6)	0.2967(4)	0.0125(6)
		s,1	0.0063(10)	-0.0025(11)	0.0008(5)	
		c,1	0.035(11)	-0.0181(11)	-0.0059(4)	
O2	1 O		0.7589(6)	0.3939(7)	0.0343(4)	0.0125(6)
		s,1	-0.0053(14)	-0.0045(11)	-0.0007(4)	
		c,1	-.0042(11)	0.0188(9)	0.0051(5)	
$Na_{0.134}Eu_{0.622}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group						
M	0.622Eu + 0.1336Na = δ_{Eu1} + 2δ_{Eu2} + 2δ_{Na}; δ_{Eu1} = 0.3834(5), o(s)Eu1 = 0.5; δ_{Na} = 0.0668(4), o(s)Na = 0.2749(1); δ_{Eu2} = 0.1193(2), o(s)Eu2 = 0.1818(1)		0.5	0.25	0.8741(7)	0.0076(7)
		s,1	-0.0112(6)	-0.0067(6)	0	
		c,1	0	0	-0.0031(9)	
Mo	1 Mo		0.5	0.25	0.3749(6)	0.0146(8)
		s,1	0.0114(8)	0.0116(9)	0	
		c,1	0	0	-0.0048(6)	
O1	1 O		0.3210(16)	0.0015(15)	0.2999(7)	0.0069(19)
		s,1	0.0063(10)	-0.0025(11)	0.0008(5)	
		c,1	0.035(11)	-0.0181(11)	-0.0059(4)	
O2	1 O		0.7658(15)	0.3850(17)	0.0296(9)	0.0069(19)
		s,1	0.004(4)	0.009(4)	-0.0077(13)	
		c,1	-.018(3)	0.033(3)	0.0123(14)	
$Na_{0.015}Eu_{0.662}MoO_4$; *I*2/*b*($\alpha\beta$0)00 (3+1)D superspace group						
M	0.6616Eu + 0.015Na = δ_{Eu1} + 2δ_{Eu2} + 2δ_{Na}; δ_{Eu1} = 0.6436(5), o(s)Eu1 = 0.5; δ_{Na} = 0.0075(1), o(s)Na = 0.1744(2) ; δ_{Eu2} = 0.009(1), o(s)Eu2 = 0.1661(2)		0.5	0.25	0.867(14)	0.0076(7)
		s,1	0.003(6)	-0.018(6)	0	
		c,1	0	0	-0.024(16)	
Mo	1 Mo		0.5	0.25	0.379(4)	0.0146(8)

		s,1	0.048(6)	0.035(6)	0	
		c,1	0	0	-0.013(4)	
O1	1 O		0.384(16)	-0.008(13)	0.284(6)	0.0069(19)
		s,1	0.01(2)	-0.018(19)	-0.006(10)	
		c,1	-0.02(2)	-0.046(17)	-0.001(1)	
O2	1 O		0.78(2)	0.42(2)	0.033(7)	0.0069(19)
		s,1	-0.037(18)	-0.03(2)	-0.010(10)	
		c,1	-.039(19)	-0.034(18)	0.006(11)	

* δ_M and o(s)*M* parameters define the length, respectively the centre coordinate x_4, for the atomic domain of *M*-cation (see Diagram S1).

Estimation of the amount of Eu atoms forming isolated Eu-clusters.

An assembling of Eu atoms continuously connected to each other by 3.95 Å distances and isolated from other Eu atoms by Na or vacancies (Δ) is called the Eu-cluster with composition $Eu_n(Na,\Delta)_k$ ($4n^{0.5} \le k \le 2(n+1)$). The shortest Eu - Eu distance is equal to about 3.95 Å within Eu-clusters, whereas the shortest Eu-Eu distance between them is longer than 5.1 Å. For $Na_{0.5}Eu_{0.5}MoO_4$ and $Na_{0.286}Eu_{0.572}MoO_4$ with statistical distribution of Eu, Na and vacancies, Δ, in the cationic *M* subset (Fig. S2), the amount of the $Eu_{cluster}$ per chemical formula unit has been estimated as a sum of probabilities p_1 and p_2 of the $Eu(Na,\Delta)_4$ and $Eu_2(Na,\Delta)_6$ clusters (Fig. S2), respectively.

Explanation: For a compound with the ratio Eu/(Na + Δ) = a/b, the probability of a cluster $Eu_n(Na,\Delta)_k$ ($4n^{0.5} \le k \le 2(n+1)$) can be expressed as $p_n = (b/(a+b))^k(a/(a+b))^{n-1}$, where n is the number of Eu in the cluster. If a/b = 1/1, then $p_n = (0.5)^m$, where $4n^{0.5}+n-1 \le m \le 3n+1$ and m is integer. Thus, the probability strongly decreases with increasing n. Therefore, only $Eu(Na,\Delta)_4$ (n = 1) and $Eu_2(Na,\Delta)_6$ (n = 2) clusters have been considered for $Na_{0.5}Eu_{0.5}MoO_4$ and $Na_{0.286}Eu_{0.572}MoO_4$. For $Na_{0.5}Eu_{0.5}MoO_4$, a/b = 1/1 and $p_1 + p_2 = (0.5)^4 + 4(0.5)^7 \approx 0.09375$. For $Na_{0.286}Eu_{0.572}MoO_4$, a/b = 4/3 and $p_1 + p_2 = (3/7)^4 + 4(3/7)^6 4/7 \approx 0.0492$. These values are included in Table S3.

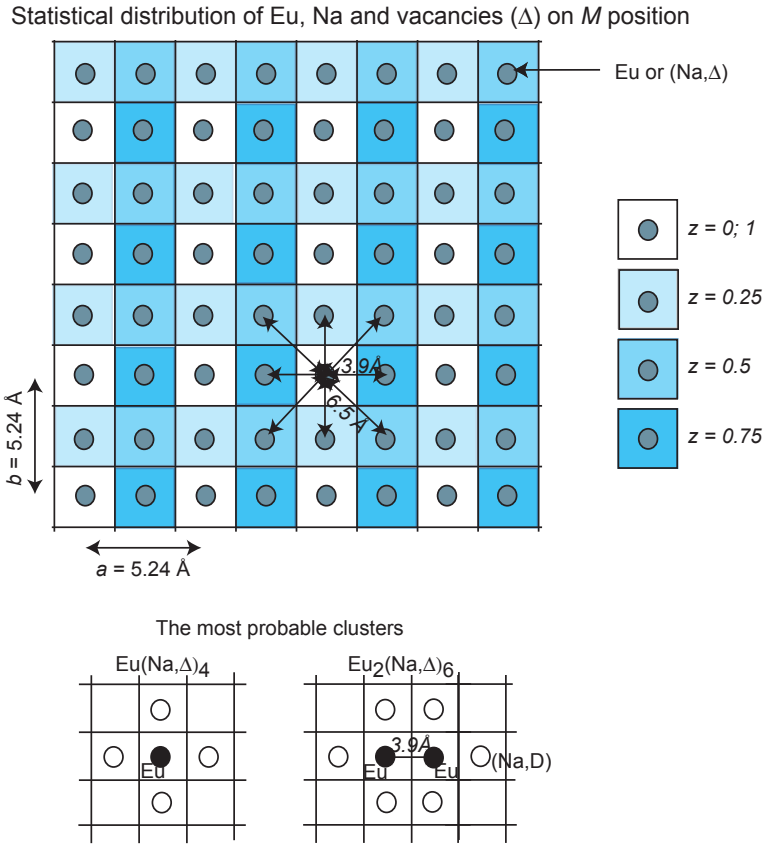

Figure S2. Schematic representation of the *ab* projection of the cationic subset in the $Na_xEu_{2/3-x/3}MoO_4$ scheelite like structures. Arrows indicate approximate values of inter-cationic distances. The most probable Eu-clusters appearing in the statistical structure are shown separately.

In the ordered incommensurately modulated structure, only di-atomic Eu-clusters, $Eu_2(Na,\Delta)_6$, are observed (Fig. S3, top). These clusters are formed by Eu1 atomic domains (Diagram S1 and Table S2). The Eu1 atoms forming $Eu_2(Na,\Delta)_6$ clusters are characterized by the unique Eu1-Eu1 distance about 3.9 Å. The portion of Eu1 atoms can be directly deduced from the *t*-plot of Eu1 – Eu distance (2*g1* in Fig. S3, bottom). However, this unique Eu1-Eu1 distance is also characteristic of another group, which is indicated as Eu1-Eu1-Eu2 in Fig. S3, top. The part of Eu1 atoms included in the latter group can be estimated as 2*g2* from the *t*-plot of Eu1-Eu distance (Fig. S3, bottom). Thus, the part of $Eu_{cluster}$ is equal to (2*g1* – 2*g2*). The corresponding values of 2*g1*, 2*g2*, (2*g1* – 2*g2*), $Eu_{cluster}$ and relative amount of $Eu_{cluster}$, $Eu_{cluster}/Eu_{total}$, are listed in Table S3.

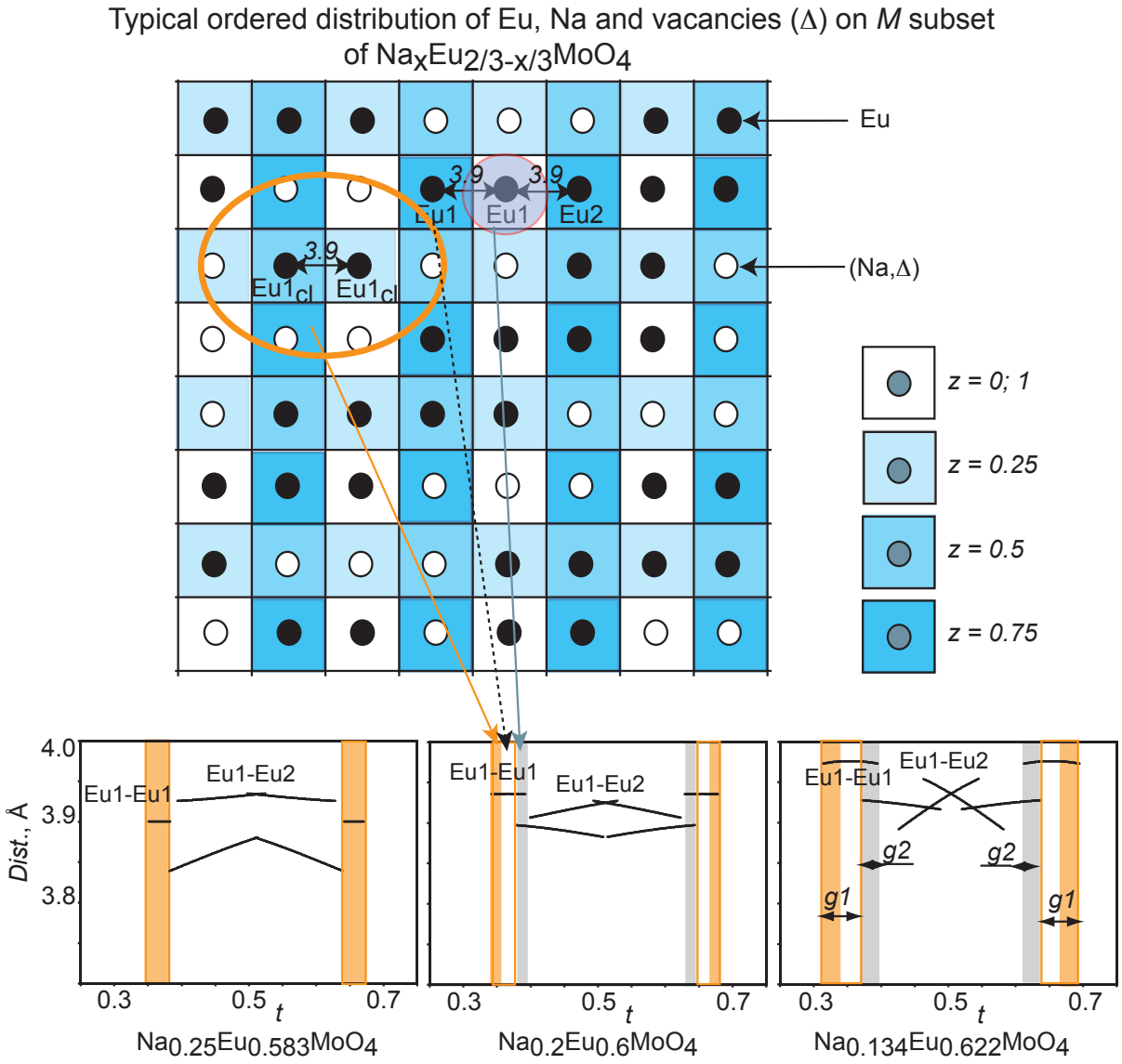

Figure S3. Schematic representation of the *ab* projection of the *M* cationic subset with a typical ordered distribution of Eu, Na and vacancies in $Na_xEu_{2/3-x/3}MoO_4$ (top), and the *t*-plot of the Eu1 – Eu distances for three compounds from the series. The typical $Eu_2(Na,\Delta)_6$ cluster (in the scheme and its relative part (in the *t*-plots) are highlighted in orange. The Eu1 – Eu1 – Eu2 group (in the scheme) with 3.9 Å Eu1 – Eu1 and Eu1 – Eu2 distances, and its relative part (in the *t*-plots) are indicated in grey. The part of Eu1 atoms with a unique Eu1 – Eu1 distance and with one Eu1 – Eu1 and one Eu1 – Eu2 distances are indicated as *g1* and *g2*, respectively, in one *t*-plot.

Table S3. Estimation of the amount of Eu atoms forming isolated Eu-clusters on the basis of Eu-Eu distances in $Na_xEu_{(2-x)/3}MoO_4$.

Refined composition	Relative part of Eu with the unique Eu1-Eu1 distance ($2g1$)	Relative part of Eu with one Eu1-Eu1 and one Eu1-Eu2 distances ($2g2$)	Relative part of $Eu_{cluster}$ ($2g1 - 2g2$)	$Eu_{cluster}/Eu_{total}$ $(2(g1-g2)/((2-x)/3) = 6(g1-g2)/(2-x))$
$Na_{0.5}Eu_{0.5}MoO_4$	----	----	0.09375 (*)	0.09375 : 0.5 ≈ 0.1875 or 18.75% (*)
$Na_{0.25}Eu_{0.583}MoO_4$	0.031(2) × 2	0.002(1) × 2	0.058(3)	10.0(5)%
$Na_{0.236}Eu_{0.588}MoO_4$	0.041(2) × 2	0.006(1) × 2	0.070(3)	11.9(5)%
$Na_{0.2}Eu_{0.6}MoO_4$	0.036(2) × 2	0.017(1) × 2	0.038(30)	6.3(5)%
$Na_{0.138}Eu_{0.621}MoO_4$	0.069(2) × 2	0.0355(1) × 2	0.067(3)	10.8(5)%
$Na_{0.134}Eu_{0.622}MoO_4$	0.057(2) × 2	0.027(1) × 2	0.06(3)	9.6(5)%
$Na_{0.286}Eu_{0.572}MoO_4$	----	----	0.0492 (*)	0.0492 : 0.572 ≈ 0.086 or 8.6% (*)

(*) For $Na_{0.5}Eu_{0.5}MoO_4$ and $Na_{0.286}Eu_{0.572}MoO_4$ with statistical distribution of Eu, Na and vacancies (Δ) in the cationic *M*-position, the relative amount of the $Eu_{cluster}$ has been estimated as a sum of probabilities p_1 and p_2 of the $Eu(Na,\Delta)_4$ and $Eu_2(Na,\Delta)_6$ clusters.

Table S4. Details of the luminescence characteristic measurements and the corresponding relative amount of the Eu-clusters for the $Na_xEu_{3+2/3-x/3}MoO_4$ compounds.

Sample No.	x	τ_{obs} (ms)[a] 293 K	τ_{obs} (ms)[a] 77 K	τ_{rad} (ms)[b]	n[c]	Q_{Eu}^{Eu} (%)[d]	Q_{Eu}^{MoO4} (%)[e]	η_{sens} (%)	$Eu_{cluster}/Eu_{total}$[f]
8	0	0.033(1)	0.102(2)	0.508	1.91	6.5	0.24	3.7	0.004
4	0.2	0.017(1) (14 %) 0.061(1) (86 %) <τ> = 0.059	0.22(2)	0.773	1.65	7.6	1.8	24	0.063
7	0.286	0.072(1)	0.27(1)	0.615	1.85	11.7	3.45	29	0.086
6	0.134	0.036(2) (6 %) 0.106(4) (94 %) <τ> = 0.105	0.30(1)	0.669	1.75	15.7	3.0	19	0.096
2	0.25	0.036(2) (8 %) 0.131(6) (92 %) <τ> = 0.129	0.33(2)	0.713	1.73	18.1	5.2	29	0.10
5	0.138	0.059(4) (8 %) 0.121(2) (92 %) <τ> = 0.118	0.33(1)	0.590	1.85	20.0	4.1	21	0.108
3	0.236	0.036(1) (8 %) 0.124(1) (92 %) <τ> = 0.122	0.33(2)	0.697	1.72	17.5	4.7	27	0.119
1	0.5	0.052(4) (6 %) 0.237(2) (94 %) <τ> = 0.234	0.38(2)	0.903	1.55	25.9	9.8	38	0.1875

[a] Measured under 355-nm laser excitation; $\langle\tau\rangle = \sum_i B_i\tau_i^2 / \sum_i B_i\tau_i$; [b] Calculated from $Q_{Eu}^{Eu} = \frac{\tau_{obs}}{\tau_{rad}}$;

[c] Calculated using $\frac{1}{\tau_{rad}} = A_{MD} n^3 \int \frac{I_{tot}}{I_{MD}}$;

[d] Measured under excitation at 464 nm; [e] Under excitation at 320 nm; [f] structural data

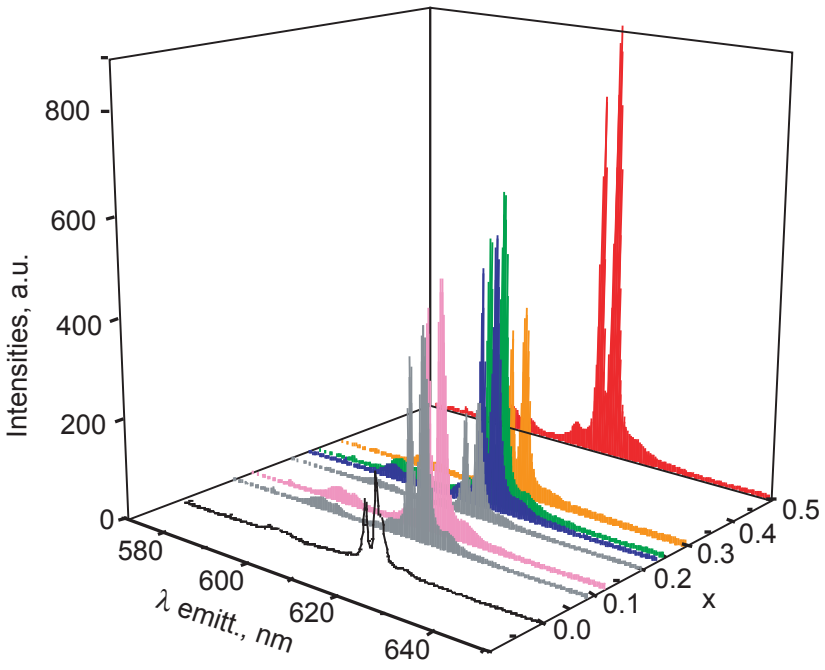

Figure S4. Relative intensities of the emission spectra as a function of composition of $Na_xEu^{3+}_{2/3-x/3}MoO_4$.