Enhanced thermoluminescence of sodium-doped lithium-magnesium fluorophosphate $Li_9Mg_3[PO_4]_4F_3$

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Supplementary information

XRPD patterns were collected at room temperature in the 2Θ range 5° to 120° with a step of 0.02°. Neutron diffraction (NPD) data were collected at room temperature in the 2Θ range 10 - 120° with a step of 0.1° and neutron wavelength λ =1.5265 Å.

The XRPD and NPD patterns of the $Li_9Mg_3[PO_4]_4F_3$ and $Li_9Mg_3[PO_4]_4F_3$: Na 2% (Fig. S1- S4) were indexed in hexagonal symmetry with unit cell parameters a = 12.63957(5) Å, c = 5.01294(3) Å, V = 693.565(5) Å^3 and a = 12.64868(5) Å, c = 5.01439(3) Å, V = 694.767(6) Å^3) respectively (Table S1).

The details of the refinements, refined atomic coordinates and temperature factors, are collected in Tables S1-S2.

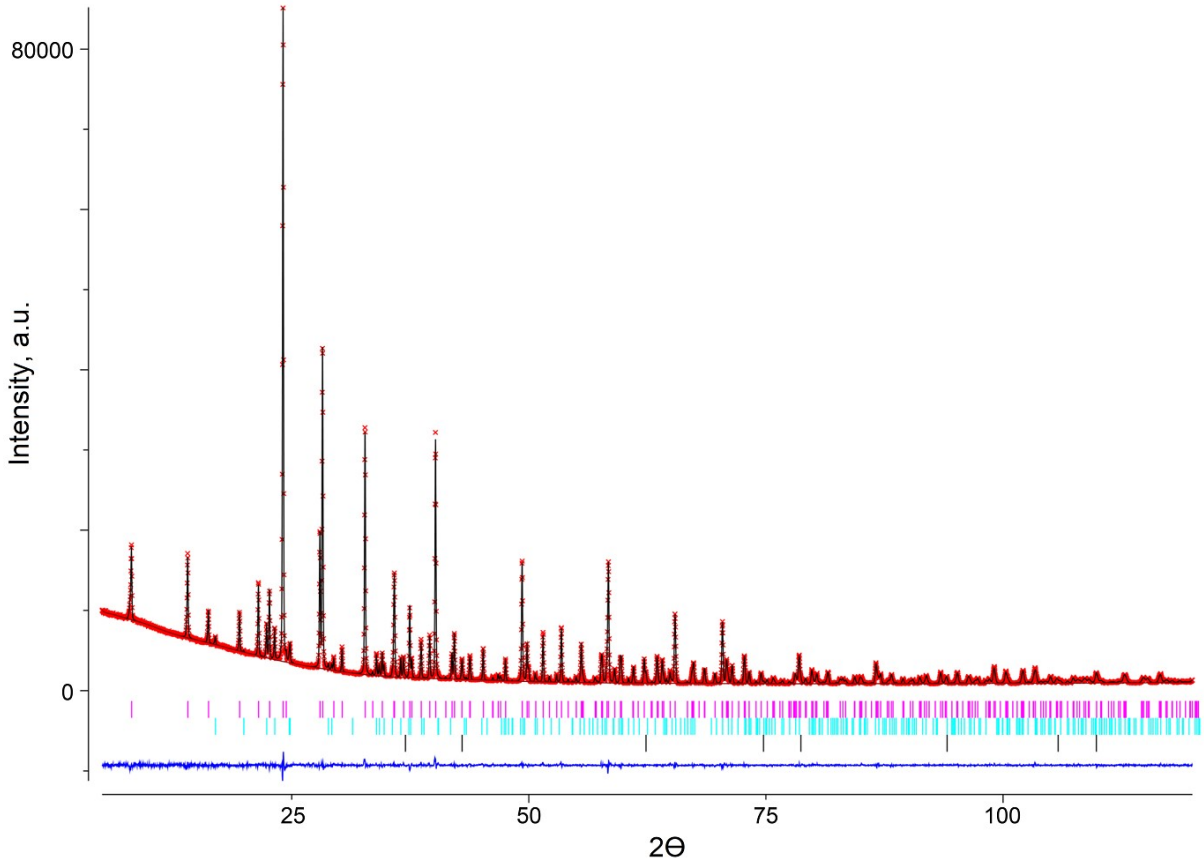

Fig. S1 Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns of $Li_9Mg_3[PO_4]_4F_3$. The series of tick marks correspond to the Bragg reflections: $Li_9Mg_3[PO_4]_4F_3$ – lilac, Li_3PO_4 – blue, MgO– black

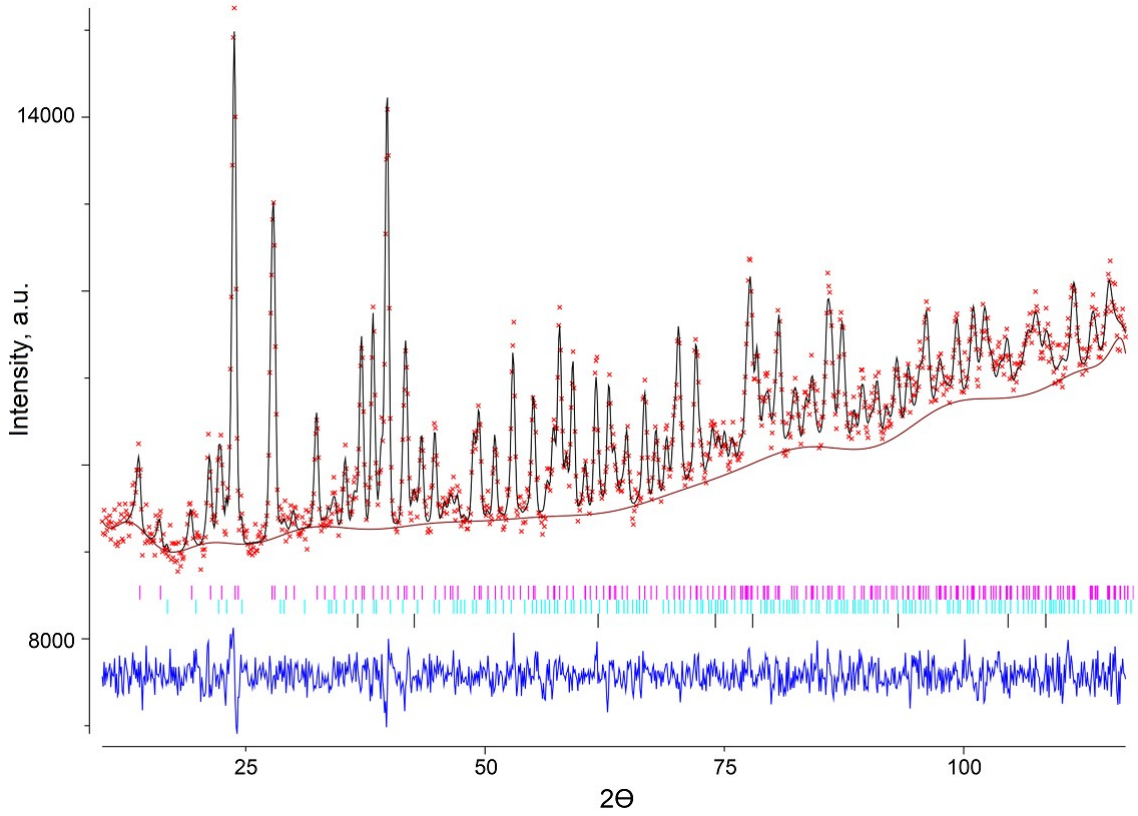

Fig. S2. Experimental (crosses), calculated (solid line), and difference (bottom line) NPD patterns of $Li_9Mg_3[PO_4]_4F_3$. The series of tick marks correspond to the Bragg reflections: $Li_9Mg_3[PO_4]_4F_3$ – lilac, Li_3PO_4 - blue, MgO – black

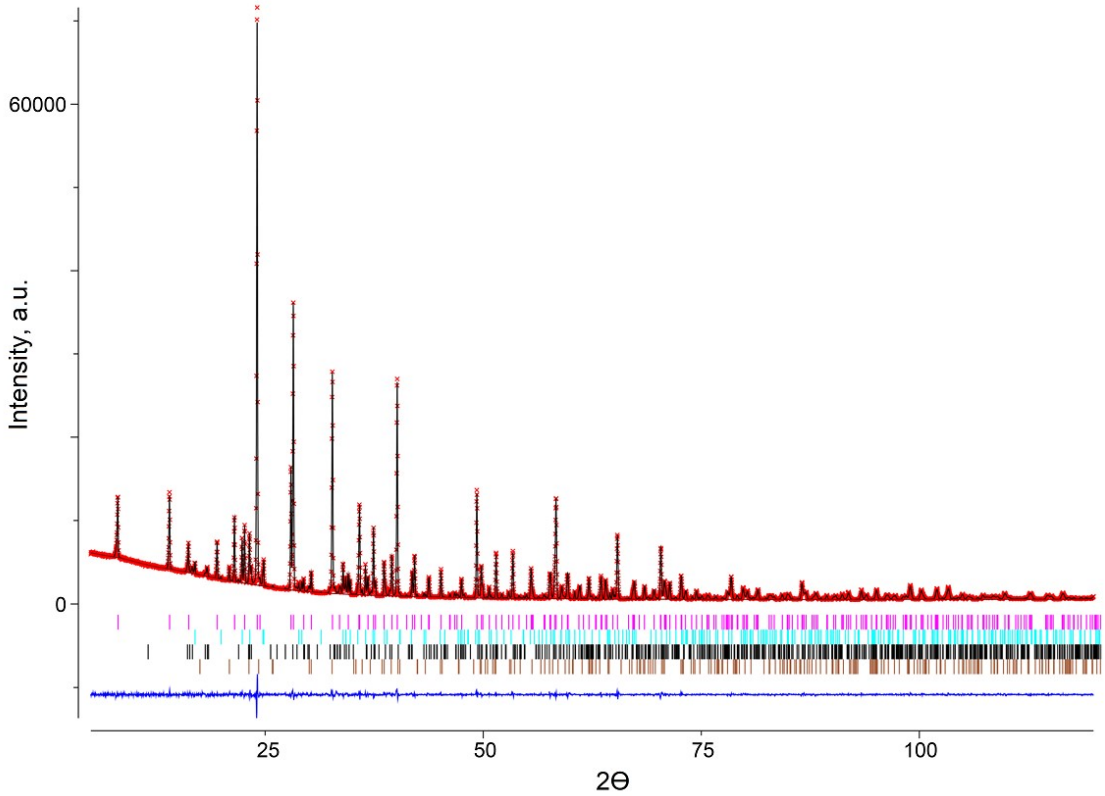

Fig. S3. Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns of $Li_9Mg_3[PO_4]_4F_3$: Na 2%. The series of tick marks correspond to the Bragg reflections: $Li_9Mg_3[PO_4]_4F_3$ – lilac, Li_3PO_4 - blue, $LiMgPO_4$ - black and Li_2MgPO_4F – brown

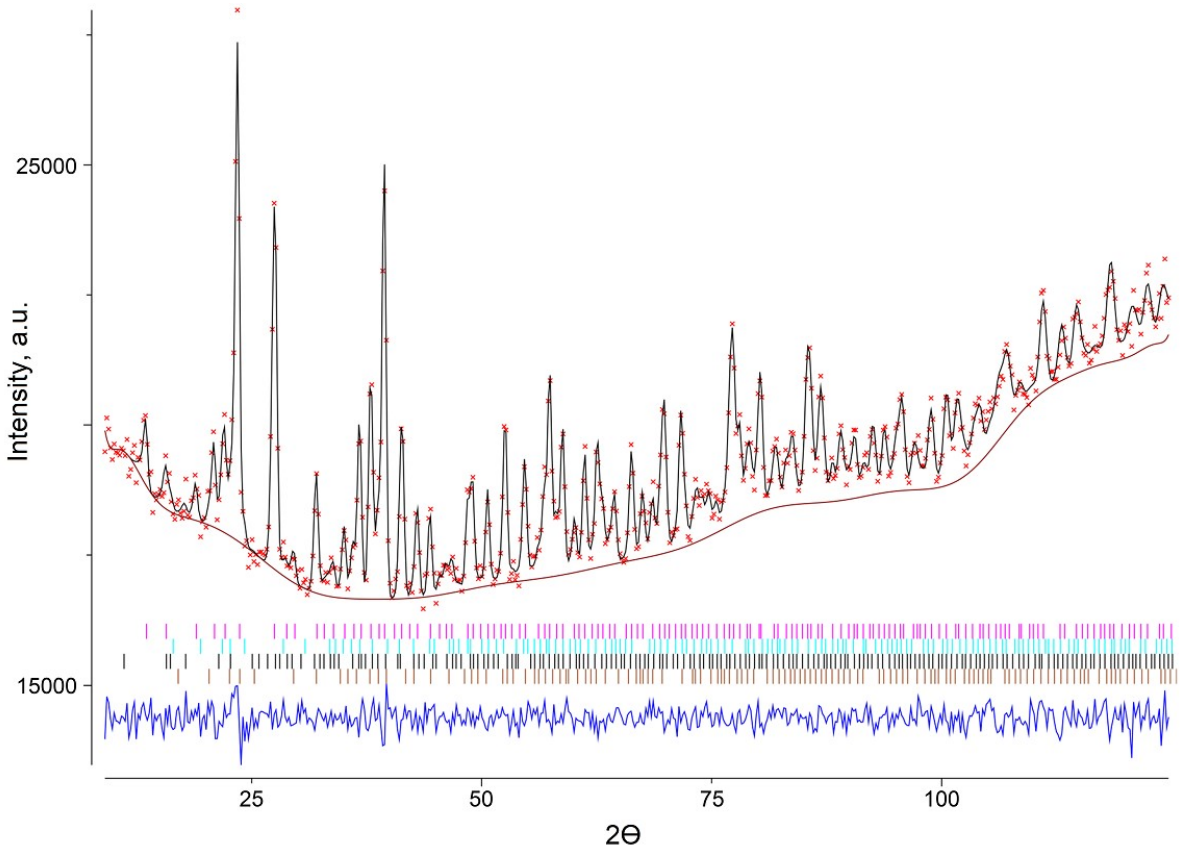

Fig. S4. Experimental (crosses), calculated (solid line), and difference (bottom line) NPD patterns of $Li_9Mg_3[PO_4]_4F_3$: Na 2%. The series of tick marks correspond to the Bragg reflections: $Li_9Mg_3[PO_4]_4F_3$ – lilac, Li_3PO_4 - blue, $LiMgPO_4$ - black and Li_2MgPO_4F – brown

Table S1. Structural data for the $Li_9Mg_3[PO_4]_4F_3$ and $Li_9Mg_3[PO_4]_4F_3$: Na 2%

Chemical formula	$Li_9Mg_3[PO_4]_4F_3$	$Li_9Mg_3[PO_4]_4F_3$: Na 2%
Crystal system	Hexagonal	Hexagonal
Space group, #	$P6_3$ (173)	$P6_3$ (173)
$a = b$, Å	12.63957(5)	12.64868(5)
c, Å	5.01294(3)	5.01439(3)
V, Å^3	693.565(5)	694.767(6)
Z	2	2
D_x, g/cm^3	2.740	2.749
R_{wp}, % (x-ray/neutrons)	2.74/1.38	3.55/0.99
R_p, % (x-ray/neutrons)	1.97/1.09	2.57/0.78
$R(F^2)$, % (x-ray/neutrons)	2.56/6.00	3.01/6.66
χ^2	2.134	2.453
Impurity, m.% (x-ray/neutrons)		

Li_3PO_4	6.4/5.5	8.9/7.7
MgO	1.4/1.7	
Li_2MgPO_4F		7.0/7.6
$LiMgPO_4$		1.1/1.7

*Table S2. Atom coordinates and isotropic thermal parameters U_{iso}*100 ($Å^2$) for the $Li_9Mg_3[PO_4]_4F_3$ and $Li_9Mg_3[PO_4]_4F_3$: Na 2%*

Atom	Wyck.	*x /a*	*y/b*	*z/c*	Fraction.	U_{iso}×100
$Li_9Mg_3[PO_4]_4F_3$						
Li1	6*c*	0.0811(8)	0.9118(8)	0.3324(15)	1	2.5(2)
Li2	6*c*	0.5732(11)	0.1699(9)	0.305(3)	1	6.9(4)
Li3	6*c*	0.4235(9)	0.0904(9)	0.765(4)	1	3.2(3)
Mg	6*c*	0.35815(14)	0.9330(2)	0.2663(9)	1	2.68(4)
P1	6*c*	0.31978(10)	0.16616(13)	0.2507(5)	1	2.76(3)
P2	2*b*	2/3	1/3	0.7901(6)	1	2.88(8)
O1	6*c*	0.5974(4)	0.3951(4)	0.6757(7)	1	2.47(8)
O2	6*c*	0.1783(2)	0.0853(3)	0.2458(7)	1	2.44(7)
O3	6*c*	0.3798(3)	0.0981(3)	0.3769(7)	1	2.59(9)
O4	6*c*	0.3577(3)	0.2849(3)	0.3967(7)	1	2.62(10)
O5	6*c*	0.3612(2)	0.1928(4)	0.9494(6)	1	2.92(9)
O6	2*b*	2/3	1/3	0.1003(10)	1	2.70(13)
F1	6*c*	0.5227(3)	0.0408(2)	0.0660(7)	1	2.98(6)
$Li_9Mg_3[PO_4]_4F_3$: Na 2%						
Li/Na1	6*c*	0.0839(9)	0.9114(9)	0.322(2)	0.951/0.049(3)	3.3(2)
Li2	6*c*	0.5718(13)	0.1628(10)	0.316(3)	1	6.3(4)
Li/Na3	6*c*	0.4271(9)	0.0940(9)	0.767(4)	0.989/0.011(3)	2.5(3)
Mg	6*c*	0.3585(2)	0.9326(2)	0.2714(8)	1	2.75(4)
P1	6*c*	0.32008(12)	0.16577(15)	0.2542	1	2.87(3)
P2	2*b*	2/3	1/3	0.7954(5)	1	2.91(8)
O1	6*c*	0.5979(4)	0.3951(4)	0.6808(7)	1	2.76(9)
O2	6*c*	0.1794(2)	0.0857(3)	0.2521(8)	1	2.83(8)
O3	6*c*	0.3792(3)	0.0978(4)	0.3842(7)	1	2.82(11)
O4	6*c*	0.3579(4)	0.2855(4)	0.3996(8)	1	3.12(12)

O5	6*c*	0.3623(3)	0.1933(4)	0.9569(5)	1	2.78(10)
O6	2*b*	2/3	1/3	0.1071(12)	1	3.29(15)
F1	6*c*	0.5213(3)	0.0386(2)	0.0710(6)	1	3.26(7)

Table S3. Selected interatomic distances d (Å) for the coordination polyhedra in $Li_9Mg_3[PO_4]_4F_3$ and $Li_9Mg_3[PO_4]_4F_3$: Na 2%

	$Li_9Mg_3[PO_4]_4F_3$	$Li_9Mg_3[PO_4]_4F_3$: Na 2%		$Li_9Mg_3[PO_4]_4F_3$	$Li_9Mg_3[PO_4]_4F_3$: Na 2%
	Distance	Distance		Distance	Distance
Li1/Na-O2	1.953(10)	1.943(10)	Mg1-O1	2.035(3)	2.036(4)
Li1/Na-O2	1.954(10)	1.977(10)	Mg1-O3	2.042(3)	2.052(4)
Li1/Na-O2	2.074(7)	2.160(9)	Mg1-O4	2.056(4)	2.068(5)
Li1/Na-O5	2.190(7)	2.194(8)	Mg1-O5	2.044(4)	2.049(4)
Average	**2.043**	**2.069**	Mg1-F1	2.088(3)	2.070(4)
Expected[a]	*1.970*	*1.990*	Mg1-F1	2.033(4)	2.037(4)
Li2-O1	1.905(16)	1.888(17)	**Average**	**2.050**	**2.052**
Li2-O3	2.171(13)	2.173(15)	*Expected[a] IV*	**2.077**	**2.077**
Li2-O4	2.670(13)	2.610(15)	*Expected[a] VI*	*2.083*	*2.083*
Li2-O6	2.067(12)	2.145(13)	P1-O2	1.555(2)	1.547(3)
Li2-F1	1.858(12)	1.839(13)	P1-O3	1.539(3)	1.538(4)
Li2-F1	2.655(12)	2.552(13)	P1-O4	1.516(4)	1.526(4)
Average IV	**2.000**	**2.011**	P1-O5	1.579(2)	1.563(3)
Average VI	**2.221**	**2.201**	**Average**	**1.547**	**1.543**
Expected[a] IV	*1.955*	*1.955*	*Expected[a] IV*	*1.545*	*1.545*
Expected[a] VI	*2.123*	*2.123*	*Expected[a] VI*	*1.550*	*1.550*
Li3/Na-O1	2.053(12)	2.011(12)	P2-O1 (3×)	1.546(2)	1.541(3)
Li3/Na-O3	2.039(19)	2.021(19)	P2-O6	1.556(6)	1.563(7)

Li3/Na-O4	2.037(12)	2.076(12)	**Average**	**1.549**	**1.547**
Li3/Na-O5	2.040(12)	2.045(12)	*Expected*[a]	*1.550*	*1.550*
Li3/Na-F1	2.241(15)	2.250(15)			
Li3/Na-F1	2.311(12)	2.303(11)			
Average	**2.120**	**2.118**			
Expected[a] *IV*	*2.117*	*2.120*			
Expected[a] *VI*	*2.123*	*2.126*			

[a] The sum of the crystal radii according to [1]: Li^{+} IV – 0.73 Å, Li^{+} VI – 0.9 Å, Na^{+} IV - 1.13 Å, Na^{+} VI - 1.16 Å, Mg^{+2} VI – 0.86 Å, P^{+5} IV – 0.31 Å, O^{-2} III – 1.22 Å, O^{-2} IV – 1.24 Å. F^{-} V – 1.18 Å (calculated by interpolation from F^{-} IV – 1.17 Å, and F^{-} VI – 1.19 Å), F^{-} VI – 1.19 Å. For Li/Na site, expected distances are calculated taking in account the fractions of lithium and sodium.

Table S4. The bond–valence sums (BVS) with % of deviation (Dev) for the cations and oxygen anions in $Li_9Mg_3[PO_4]_4F_3$ and $Li_9Mg_3[PO_4]_4F_3$: Na 2%

		$Li_9Mg_3[PO_4]_4F_3$		$Li_9Mg_3[PO_4]_4F_3$: Na 2%	
Atom	Assumed oxidation state	BVS	% deviation	BVS	% deviation
Li1/Na	1	0.869	13	0.894	11
Li2	1	0.98	2	0.988	1
Li3/Na	1	1.013	1	1.037	4
Mg1	2	2.093	5	2.074	4
P1	5	4.839	3	4.886	2
P2	5	4.815	4	4.841	3
O1	2	2.119	6	2.173	9
O2	2	1.91	5	1.892	5
O3	2	1.986	1	1.988	1
O4	2	1.942	3	1.88	6
O5	2	1.848	8	1.887	6
O6	2	1.77	11	1.637	18
F1	1	1.004	0	1.037	4
Global Instability Index		0.12		0.14	

References

[1] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr.*, 1976, A32, 751–767. https://doi.org/10.1107/S0567739476001551.