Supplementary Information

Polymorphism and polymorph-dependent luminescence properties of the first lithium oxonitridolithosilicate Li_3SiNO_2:Eu^{2+}

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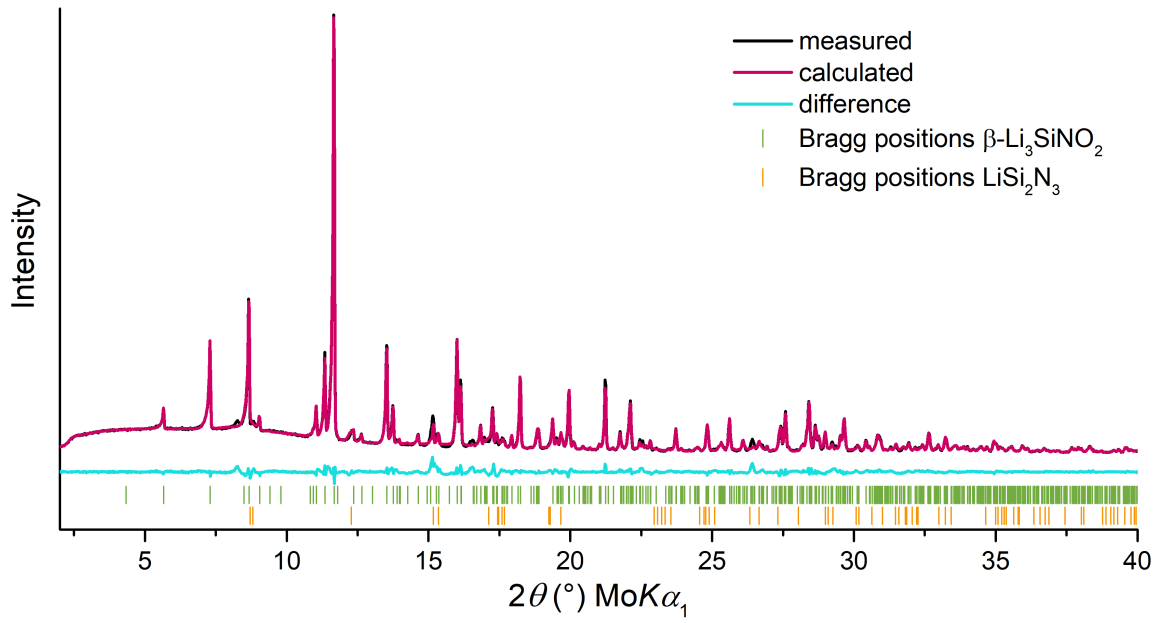


Figure S1: Rietveld refinement of the X-ray diffraction data from a powder sample of β-Li_3SiNO_2. The measured pattern is shown in black, the calculated pattern in red, the difference curve in turquiose and the tick marks of the

theoretical positions for the reflections are shown in green for β-Li_3SiNO_2 and in orange for the side phase $LiSi_2N_3$.

Table S1: Report of the Rietveld refinements of the powder X-ray diffraction data from undoped and doped β-Li_3SiNO_2 samples.

Parameter	***Value (undoped sample)***	***Value (doped sample)***
Phase composition		
β-Li_3SiNO_2 /wt%	95.1(2)	93.7(6)
$LiSi_2N_3$ /wt%	4.9(2)	6.3(6)
Powder diffraction data of β-Li_3SiNO_2		
Diffractometer	STOE STADI P	
Radiation; wavelength /Å	Mo-Kα_1; 0.7093	
a /Å	18.7462(5)	18.7451(7)
b /Å	11.1270(4)	11.1254(5)
c /Å	5.0897(2)	5.0916(2)
Cell volume /Å^3	1061.66(5)	1061.83(7)
2θ range / °	2 – 40	2 – 42
2θ step width / °	0.015	0.015
R_{exp} /%	1.78	5.31
R_{wp} /%	6.14	8.40
R_p /%	3.91	6.25
R_{Bragg} /%	2.10	2.733

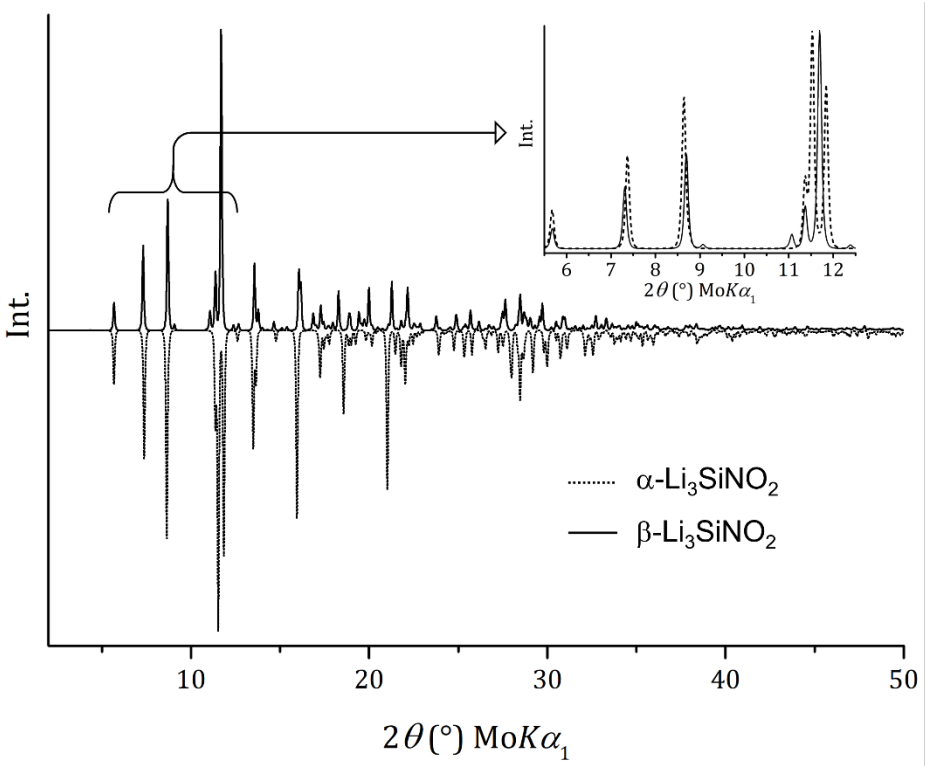


Figure S2: Comparison of the powder X-ray diffraction patterns for α- (negative values/ dotted line) and β-Li_3SiNO_2 (positive values/ solid line). The inset shows similarities and significant differences between the polymorphs in the lower diffraction angles.

Table S2: Wyckoff positions, atomic coordinates, and equivalent isotropic displacement parameters U_{eq} (Å²) of orthorhombic β-Li_3SiNO_2 (standard deviations in parentheses).

Atom	Wyckoff-Position	x	y	z	U_{eq}	occ.
Si1	8c	0.98497(2)	0.67981(5)	0.77906(9)	0.0141(2)	1
Si2	8c	0.76186(2)	0.67932(4)	0.17254(9)	0.0143(2)	1
O1	8c	0.93834(6)	0.5624(2)	0.6621(2)	0.0162(3)	1
O2	8c	0.80929(6)	0.5616(2)	0.2823(2)	0.0174(4)	1
O3	8c	0.92995(6)	0.3576(2)	0.2544(3)	0.0273(5)	1
O4	8c	0.67788(7)	0.6406(2)	0.2236(3)	0.0295(5)	1
N1	8c	0.96028(8)	0.6952(2)	0.1019(3)	0.0186(4)	1
N2	8c	0.78621(8)	0.6951(2)	0.8473(3)	0.0183(4)	1
Li1	8c	0.8728(2)	0.4583(2)	0.4744(4)	0.034(2)	0.9854(7)
Eu1	8c	0.8728(2)	0.4583(2)	0.4744(4)	0.000026(2)	0.0146(7)
Li2	8c	0.8783(2)	0.2303(3)	0.4774(5)	0.052(3)	0.9888(8)
Eu2	8c	0.8783(2)	0.2303(3)	0.4774(5)	0.000031(3)	0.0112(8)
Li3	8c	0.8737(2)	0.6836(3)	0.4728(7)	0.029(2)	1
Li4	8c	0.8716(2)	0.5747(5)	0.9658(9)	0.0279(9)	0.78
Li4a	8c	0.8733(8)	0.518(2)	0.964(3)	0.028(3)	0.22
Li5	8c	0.0144(2)	0.4493(3)	0.6988(7)	0.035(2)	1
Li6	8c	0.7488(2)	0.4395(3)	0.1271(7)	0.032(2)	1

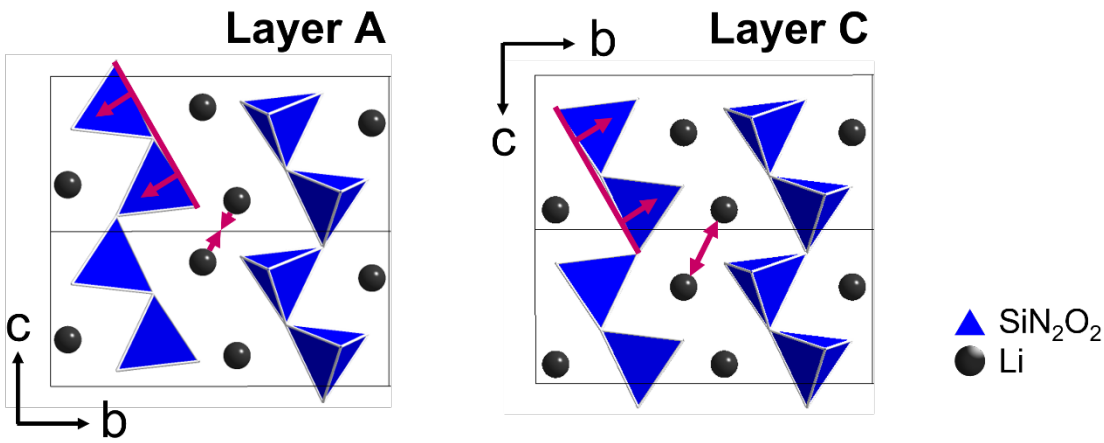
Table S3: Anisotropic displacement parameters U_{ij} (Å²) of orthorhombic β-Li_3SiNO_2 (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si1	0.0158(2)	0.0133(2)	0.0132(2)	-0.0002(2)	-0.0007(2)	-0.0008(2)
Si2	0.0164(2)	0.0129(2)	0.0135(2)	-0.0006(2)	0.0003(2)	-0.0001(2)
O1	0.0175(6)	0.0137(6)	0.0173(6)	0.0002(4)	0.0002(5)	-0.0017(4)
O2	0.0208(6)	0.0140(6)	0.0173(6)	-0.0017(5)	-0.0035(5)	0.0006(4)
O3	0.0181(7)	0.0300(9)	0.0337(8)	-0.0006(5)	0.0000(6)	-0.0100(6)
O4	0.0228(7)	0.0336(9)	0.0322(8)	-0.0046(6)	0.0044(6)	-0.0073(6)
N1	0.0280(7)	0.0138(7)	0.0139(7)	0.0001(6)	0.0006(6)	0.0011(5)
N2	0.0281(7)	0.0142(7)	0.0126(7)	0.0005(6)	-0.0020(6)	0.0001(5)
Li1	0.036(3)	0.038(3)	0.028(3)	0.003(2)	0.001(2)	0.003(2)

Li2	0.044(4)	0.062(6)	0.050(5)	-0.020(2)	-0.018(2)	0.018(2)
Li3	0.027(2)	0.016(2)	0.043(2)	0.000(2)	-0.018(2)	-0.001(2)
Li5	0.058(2)	0.029(2)	0.016(2)	0.027(2)	-0.001(2)	0.005(2)
Li6	0.048(2)	0.018(2)	0.026(2)	-0.014(2)	-0.014(2)	0.005(2)

Table S4: Interatomic distances of orthorhombic β-Li_3SiNO_2 (standard deviations in parentheses).

Si1	– N1	1.716(2)		
	– N1	1.720(2)	Ø Si1–N	1.718
	– O1	1.680(2)		
	– O3	1.656(2)	Ø Si1–O	1.668
Si2	– N2	1.726(2)		
	– N2	1.718(2)	Ø Si2–N	1.722
	– O2	1.678(2)		
	– O4	1.652(2)	Ø Si2–O	1.665
Li1	– O1	1.941(3)		
	– O2	1.922(3)		
	– O3	1.912(3)		
	– O4	1.929(3)	Ø Li1–O	1.926
Li2	– O3	1.970(4)		
	– O3	2.056(4)		
	– O4	1.943(4)		
	– O4	2.178(4)	Ø Li2–O	2.037
Li3	– N1	2.210(4)		
	– N1	2.493(4)		
	– N2	2.216(4)		
	– N2	2.517(4)	Ø Li3–N	2.359
	– O1	2.053(4)		
	– O2	2.058(4)	Ø Li3–O	2,056
Li4	– N1	2.245(5)		
	– N2	2.172(5)	Ø Li4–N	2.209
	– O1	1.993(5)		
	– O2	1.995(5)		
	– O3	3.03(6)		
	– O4	2.85(6)	Ø Li4–O	2.47
Li4a	– N1	2.65(2)		
	– N2	2.63(2)	Ø Li4a–N	2.64
	– O1	2.02(2)		
	– O2	2.07(2)		
	– O3	2.55(2)		
	– O4	2.35(2)	Ø Li4a–O	2.25
Li5	– N1	1.960(4)		
	– O1	1.910(4)		



	– O1	2.043(4)		
	– O3	2.400(4)	Ø Li5–O	2.118
Li6	– N2	1.983(4)		
	– O2	1.938(4)		
	– O2	2.065(4)		
	– O4	2.627(4)		
	– O4	2.649(4)	Ø Li6–O	2.320

Figure S3: Comparison of excerpts of layer A (left) and C (right) of β-Li_3SiNO_2 with the differences relevant to the changed connection scheme marked in red. For clarity, the anions are not shown here.

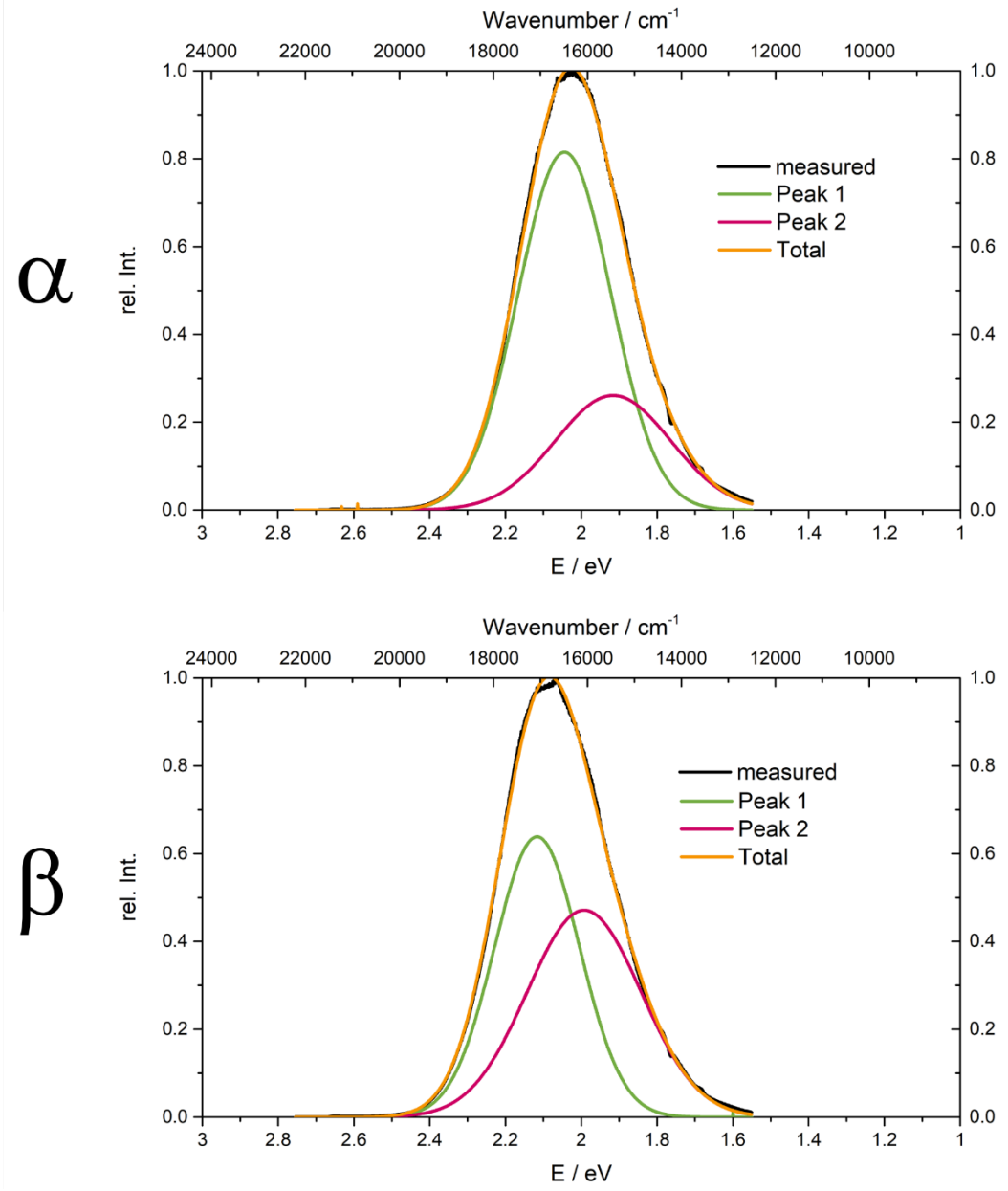


Figure S4: Bimodal Gauß-fits of the emission spectra obtained from powder samples of α- and β-Li_3SiNO_2:Eu^{2+}.

Table S5: Parameters of the two Gauß-curves of the decomposition of the emission spectra from powder samples of α- and β-Li_3SiNO_2:Eu^{2+}.

	α-Li_3SiNO_2		**β-Li_3SiNO_2**	
	Peak 1	*Peak 2*	*Peak 1*	*Peak 2*
rel. Intensity	0.72	0.28	0.50	0.50
E_{peak} / eV	2.04	1.92	2.12	1.99
$\tilde{\nu}_{peak}$ / cm^{-1}	16488	15456	17072	16071
FWHM / eV	0.29	0.36	0.26	0.35
FWHM / cm^{-1}	2323	2886	2130	2850

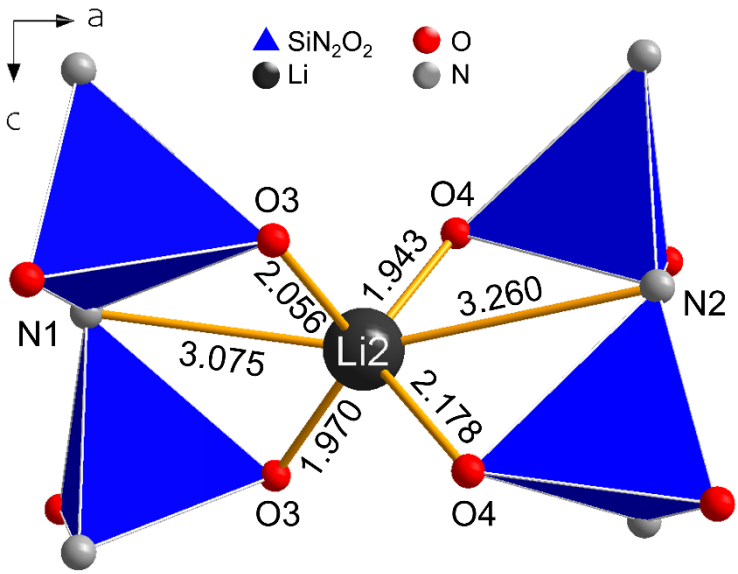


Figure S5: The local environment of the Li2-position in β-Li_3SiNO_2:$Eu^{2+}$is shown with its bond lengths in a 4+2 coordination.