Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Highlights on the reversible nonpolar-to-polar $P3_121$-$P3_1$ phase transition at low temperature in $NaLa(SO_4)_2.H_2O$: mechanism and piezoelectric properties

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Table S1: Crystal data collection and structure refinement for $NaLa(SO_4)_2.H_2O$ at 100K

Chemical formula	$H_{0.67}La_{0.33}Na_{0.33}O_3S_{0.67}$	
Formula weight	124.01 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	$P3_1$	
Unit cell dimensions	a = 7.0227(5) Å	α = 90°
	b = 7.0227(5) Å	β = 90°
	c = 12.9450(13) Å	γ = 120°
Volume	552.89(10) $Å^3$	
Z	3	
Density (calculated)	1.117 g/cm^3	
Absorption coefficient	2.148 mm^{-1}	
F(000)	174	
Theta range for data collection	3.15 to 52.27°	
Index ranges	-15<=h<=15, -15<=k<=15, -28<=l<=28	
Reflections collected	27080	
Independent reflections	8289 [R(int) = 0.0342]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8289 / 1 / 120	
Goodness-of-fit on F^2	1.041	
Final R indices	8289 data; I>2σ(I)	R1 = 0.0150, wR2 = 0.0351
	all data	R1 = 0.0150, wR2 = 0.0351

Weighting scheme	$w=1/[\sigma^2(F_o^2)]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.005(4)
Extinction coefficient	0.0220(10)
Largest diff. peak and hole	1.774 and -0.961 eÅ^{-3}

Table S2: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $NaLa(SO_4)_2.H_2O$ at 100K

	x/a	y/b	z/c	U(eq)
La01	0.57677(2)	0.01318(2)	0.49361(2)	0.00218(10)
Na02	0.4649(2)	0.47075(16)	0.65869(8)	0.00657(12)
S003	0.01571(10)	0.57106(6)	0.57995(3)	0.00283(6)
S004	0.45530(10)	0.44530(10)	0.40693(3)	0.00282(7)
O001	0.8805(2)	0.6349(2)	0.64441(10)	0.00602(15)
O002	0.1800(2)	0.7643(2)	0.52274(10)	0.00682(17)
O003	0.8786(2)	0.4022(2)	0.50378(10)	0.00670(17)
O004	0.6349(2)	0.4846(3)	0.33468(10)	0.00673(18)
O005	0.5201(2)	0.6327(2)	0.47642(10)	0.00683(17)
O006	0.1200(3)	0.4889(2)	0.65298(10)	0.00572(15)
O007	0.2671(2)	0.4084(2)	0.34166(9)	0.00582(15)
O008	0.3956(2)	0.2495(2)	0.47172(10)	0.00674(16)
O009	0.9344(3)	0.0196(3)	0.52408(14)	0.0124(2)

Table S3: Bond lengths (Å) for $NaLa(SO_4)_2.H_2O$ at 100K
(With the Symmetry transformations : #1= x, y+1, z. #2= x+1, y, z. #3= x+1, y+1, z. #4= y+1, x-y, z+1/3. #5= -y+1, x-y+1, z+1/3 #6=-x+y, -x+1, z-1/3 . #7= -x+y+1, -x+2, z-1/3)

La01-O002	2.4677(14)	La01-O003#3	2.4867(15)
La01-O005	2.5072(14)	La01-O009	2.5200(16)
La01-O008#1	2.5620(14)	La01-O004#5	2.5738(14)
La01-O006#6	2.5908(13)	La01-O001#6	2.6013(13)
La01-O007#5	2.6104(13)	La01-S004#5	3.1962(7)
La01-S003#6	3.2026(7)	La01-Na02#7	4.0263(13)
Na02-O007#5	2.4154(17)	Na02-O004#4	2.4499(17)
Na02-O003#5	2.4838(17)	Na02-O006	2.4895(19)
Na02-O001#2	2.5524(17)	Na02-O005	2.5631(17)
Na02-O008	2.7845(18)	Na02-O002#5	2.9406(18)
Na02-S004	3.2628(11)	Na02-S003#5	3.3034(11)
S003-O002	1.4681(14)	S003-O003	1.4709(14)
S003-O006	1.4785(14)	S003-O001	1.4918(14)
S004-O005	1.4658(14)	S004-O007	1.4785(14)
S004-O004	1.4811(15)	S004-O008	1.4812(14)

Table S4: Bond angles (°) for $NaLa(SO_4)_2.H_2O$ at 100K

(With the Symmetry transformations: #1= x-1, y-1, z . #2= x-1, y, z . #3= x, y-1, z . #4= x, y+1, z. #5= x+1, y, z . #6= x+1, y+1, z . #7= -y+1, x-y, z+1/3 . #8= -y+1, x-y+1, z+1/3. #9= -y+2, x-y+1, z+1/3. #10=-x+y, -x+1, z-1/3. #11= -x+y+1, -x+1, z-1/3. #12= -x+y+1, -x+2, z-1/3)

O002-La01-O003#6	144.14(5)	O002-La01-O005	74.77(5)
O003#6-La01-O005	140.32(5)	O002-La01-O009	138.66(5)
O003#6-La01-O009	71.19(6)	O005-La01-O009	70.04(5)
O002-La01-O008#4	74.06(4)	O003#6-La01-O008#4	73.78(5)
O005-La01-O008#4	144.59(5)	O009-La01-O008#4	144.96(5)
O002-La01-O004#8	77.89(5)	O003#6-La01-O004#8	75.68(5)
O005-La01-O004#8	120.64(4)	O009-La01-O004#8	101.99(5)
O008#4-La01-O004#8	67.94(4)	O002-La01-O006#10	69.16(4)
O003#6-La01-O006#10	117.36(4)	O005-La01-O006#10	77.14(5)
O009-La01-O006#10	121.27(5)	O008#4-La01-O006#10	76.41(5)
O004#8-La01-O006#10	136.72(4)	O002-La01-O001#10	123.49(4)
O003#6-La01-O001#10	73.12(4)	O005-La01-O001#10	91.32(4)
O009-La01-O001#10	78.83(5)	O008#4-La01-O001#10	92.05(4)
O004#8-La01-O001#10	146.65(5)	O006#10-La01-O001#10	54.33(4)
O002-La01-O007#8	80.43(4)	O003#6-La01-O007#8	102.70(4)
O005-La01-O007#8	69.81(4)	O009-La01-O007#8	67.67(5)
O008#4-La01-O007#8	120.31(4)	O004#8-La01-O007#8	54.23(4)
O006#10-La01-O007#8	139.83(5)	O001#10-La01-O007#8	145.41(4)
O002-La01-S004#8	78.98(3)	O003#6-La01-S004#8	88.08(3)
O005-La01-S004#8	95.74(3)	O009-La01-S004#8	83.58(4)
O008#4-La01-S004#8	94.42(3)	O004#8-La01-S004#8	27.10(3)
O006#10-La01-S004#8	148.12(3)	O001#10-La01-S004#8	157.53(3)
O007#8-La01-S004#8	27.18(3)	O002-La01-S003#10	96.14(3)
O003#6-La01-S003#10	96.30(3)	O005-La01-S003#10	82.32(3)
O009-La01-S003#10	99.92(4)	O008#4-La01-S003#10	84.71(3)
O004#8-La01-S003#10	152.63(3)	O006#10-La01-S003#10	27.02(3)
O001#10-La01-S003#10	27.36(3)	O007#8-La01-S003#10	151.89(3)
S004#8-La01-S003#10	175.087(9)	O002-La01-Na02#12	142.51(4)
O003#6-La01-Na02#12	35.87(3)	O005-La01-Na02#12	124.74(4)
O009-La01-Na02#12	77.46(4)	O008#4-La01-Na02#12	74.84(3)
O004#8-La01-Na02#12	108.84(4)	O006#10-La01-Na02#12	83.60(4)
O001#10-La01-Na02#12	38.19(3)	O007#8-La01-Na02#12	134.24(4)
S004#8-La01-Na02#12	123.941(18)	S003#10-La01-Na02#12	60.51(2)
O007#8-Na02-O004#7	152.98(7)	O007#8-Na02-O003#8	88.70(6)

O004#7-Na02-O003#8	75.12(6)	O007#8-Na02-O006	76.35(6)
O004#7-Na02-O006	129.78(7)	O003#8-Na02-O006	113.21(6)
O007#8-Na02-O001#5	78.68(5)	O004#7-Na02-O001#5	76.15(6)
O003#8-Na02-O001#5	74.02(6)	O006-Na02-O001#5	153.72(7)
O007#8-Na02-O005	72.02(5)	O004#7-Na02-O005	113.18(6)
O003#8-Na02-O005	151.25(7)	O006-Na02-O005	83.40(6)
O001#5-Na02-O005	81.25(5)	O007#8-Na02-O008	124.64(6)
O004#7-Na02-O008	66.13(5)	O003#8-Na02-O008	140.95(7)
O006-Na02-O008	95.72(6)	O001#5-Na02-O008	91.75(6)
O005-Na02-O008	52.62(5)	O007#8-Na02-O002#8	86.61(5)
O004#7-Na02-O002#8	99.08(5)	O003#8-Na02-O002#8	51.00(5)
O006-Na02-O002#8	63.24(5)	O001#5-Na02-O002#8	123.33(6)
O005-Na02-O002#8	144.05(7)	O008-Na02-O002#8	138.64(5)
O007#8-Na02-S004	97.75(5)	O004#7-Na02-S004	90.42(5)
O003#8-Na02-S004	157.98(6)	O006-Na02-S004	88.80(4)
O001#5-Na02-S004	86.57(4)	O005-Na02-S004	25.74(3)
O008-Na02-S004	26.89(3)	O002#8-Na02-S004	149.96(5)
O007#8-Na02-S003#8	87.15(4)	O004#7-Na02-S003#8	86.68(4)
O003#8-Na02-S003#8	24.62(3)	O006-Na02-S003#8	89.03(5)
O001#5-Na02-S003#8	97.81(5)	O005-Na02-S003#8	158.97(5)
O008-Na02-S003#8	148.11(5)	O002#8-Na02-S003#8	26.39(3)
S004-Na02-S003#8	174.02(4)	O007#8-Na02-La01#9	88.74(5)
O004#7-Na02-La01#9	65.42(4)	O003#8-Na02-La01#9	35.92(4)
O006-Na02-La01#9	146.92(5)	O001#5-Na02-La01#9	39.06(3)
O005-Na02-La01#9	120.18(5)	O008-Na02-La01#9	116.85(5)
O002#8-Na02-La01#9	86.87(4)	S004-Na02-La01#9	122.78(4)
S003#8-Na02-La01#9	60.50(2)	O007#8-Na02-La01	37.22(3)
O004#7-Na02-La01	146.43(5)	O003#8-Na02-La01	125.16(5)
O006-Na02-La01	71.04(4)	O001#5-Na02-La01	84.12(4)
O005-Na02-La01	35.83(3)	O008-Na02-La01	87.95(4)
O002#8-Na02-La01	114.47(4)	S004-Na02-La01	61.17(2)
S003#8-Na02-La01	123.17(3)	La01#9-Na02-La01	113.38(3)
O002-S003-O003	107.58(9)	O002-S003-O006	111.67(9)
O003-S003-O006	111.50(9)	O002-S003-O001	109.19(8)
O003-S003-O001	111.02(9)	O006-S003-O001	105.89(8)
O002-S003-La01#8	122.20(6)	O003-S003-La01#8	130.20(6)
O006-S003-La01#8	52.77(6)	O001-S003-La01#8	53.26(5)
O002-S003-Na02#10	62.89(6)	O003-S003-Na02#10	44.71(6)
O006-S003-Na02#10	127.13(6)	O001-S003-Na02#10	126.08(6)

La01#8-S003-Na02#10	174.90(3)	O005-S004-O007	110.93(8)
O005-S004-O004	111.54(10)	O007-S004-O004	105.97(9)
O005-S004-O008	107.62(9)	O007-S004-O008	110.34(9)
O004-S004-O008	110.47(9)	O005-S004-La01#10	130.04(6)
O007-S004-La01#10	53.76(5)	O004-S004-La01#10	52.34(6)
O008-S004-La01#10	122.35(6)	O005-S004-Na02	49.40(6)
O007-S004-Na02	124.94(6)	O004-S004-Na02	128.92(6)
O008-S004-Na02	58.25(6)	La01#10-S004-Na02	178.59(3)
S003-O001-Na02#2	131.35(8)	S003-O001-La01#8	99.38(7)
Na02#2-O001-La01#8	102.75(5)	S003-O002-La01	144.99(9)
S003-O002-Na02#10	90.73(7)	La01-O002-Na02#10	105.57(5)
S003-O003-Na02#10	110.67(8)	S003-O003-La01#1	140.89(8)
Na02#10-O003-La01#1	108.20(5)	S004-O004-Na02#11	143.40(9)
S004-O004-La01#10	100.56(7)	Na02#11-O004-La01#10	115.39(6)
S004-O005-La01	145.47(8)	S004-O005-Na02	104.86(8)
La01-O005-Na02	107.42(5)	S003-O006-Na02	136.35(9)
S003-O006-La01#8	100.21(7)	Na02-O006-La01#8	116.33(6)
S004-O007-Na02#10	139.69(9)	S004-O007-La01#10	99.06(7)
Na02#10-O007-La01#10	108.75(5)	S004-O008-La01#3	131.48(8)
S004-O008-Na02	94.86(7)	La01#3-O008-Na02	105.10(5)

Table S5: Anisotropic atomic displacement parameters ($Å^2$) for $NaLa(SO_4)_2.H_2O$ at 100K

	U_{11}	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
La01	0.00257(3)	0.00165(3)	0.00199(2)	0.00000(2)	0.00016(2)	0.00080(2)
Na02	0.0080(4)	0.0068(2)	0.00599(18)	-0.0003(3)	-0.0009(2)	0.0045(3)
S003	0.00262(14)	0.00273(15)	0.00280(14)	0.00015(8)	0.00016(13)	0.00107(11)
S004	0.00369(13)	0.00293(15)	0.00236(12)	0.00001(11)	-0.00010(12)	0.00205(10)
O001	0.0060(4)	0.0084(4)	0.0055(3)	0.0001(3)	0.0012(3)	0.0051(3)
O002	0.0054(4)	0.0052(4)	0.0079(4)	0.0025(3)	0.0022(3)	0.0011(3)
O003	0.0066(4)	0.0059(4)	0.0051(3)	-0.0017(3)	-0.0025(3)	0.0013(3)
O004	0.0050(4)	0.0112(5)	0.0046(3)	0.0002(3)	0.0011(3)	0.0045(4)
O005	0.0108(5)	0.0057(4)	0.0057(3)	-0.0031(3)	-0.0027(3)	0.0053(4)
O006	0.0066(4)	0.0077(4)	0.0046(3)	0.0006(3)	-0.0002(3)	0.0049(4)
O007	0.0043(4)	0.0085(4)	0.0053(3)	-0.0005(3)	-0.0017(3)	0.0037(3)
O008	0.0080(4)	0.0048(4)	0.0078(3)	0.0030(3)	0.0003(3)	0.0034(3)
O009	0.0069(4)	0.0096(6)	0.0214(6)	0.0057(5)	0.0018(4)	0.0047(4)

Figure S1: Experimental mid-infrared spectra between 1800 and 3000 cm^{-1} as a function of temperature