

## Highlights on the reversible nonpolar-to-polar P3121–P31 phase transition at low temperature in NaLa(SO4) $2 \times$ H2O: mechanism and piezoelectric properties

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H Azeroual, J-L Bantignies, D Maurin, D Granier, J Haines, et al.. Highlights on the reversible nonpolar-to-polar P3121–P31 phase transition at low temperature in NaLa(SO4)2×H2O: mechanism and piezoelectric properties. Physical Chemistry Chemical Physics, 2023, 25 (11), pp.8168 - 8179. 10.1039/d3cp00587a . hal-04052485

## HAL Id: hal-04052485 https://hal.science/hal-04052485

Submitted on 30 Mar 2023

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Cite this: DOI: 00.0000/xxxxxxxxx

## Highlights on the reversible nonpolar-to-polar $P3_121-P3_1$ phase transition at low temperature in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O: mechanism and piezoelectric properties<sup>†</sup>

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We report the existence in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O of a displacive phase transition under 200 K from the nonpolar P3<sub>1</sub>21 to the polar P3<sub>1</sub> space group. This phase transition was predicted by density functional theory based calculations and experimentally confirmed from infrared spectroscopy and xray diffraction. The A<sub>2</sub> polar irreducible representation is the primary order parameter. The structural water and hydrogen bonding are the mechanism driving the phase transition. The piezoelectric properties of this new P3<sub>1</sub> phase have been investigated by first principles based calculations. The highest piezoelectric-strain constants in the zero Kelvin limit are predicted for the d<sub>12</sub> and d<sub>41</sub> elements with values about 3.4 pC/N. This compound could be interesting as piezoelectric actuator for cryogenic applications.

#### 1 Introduction

Received Date Accepted Date

DOI:00.0000/xxxxxxxxx

Published on 27 February 2023. Downloaded by University of Montpellier on 2/28/2023 1:21:49 PM.

 $\alpha$ -Quartz crystallizes in the trigonal P3<sub>1</sub>21 (or P3<sub>2</sub>21) space group with corner-sharing SiO<sub>4</sub> tetrahedra aligned along the *c*axis. This compound is widely involved in piezoelectric applications despite a small electromechanical coupling  $(k \sim 8\%)^{1}$  and piezoelectric-strain constant  $(d_{11} = 2.5 \text{ pC/N})^2$ . Furthermore, the existence of a phase transition near 846 K to a weakly piezoelectric structure ( $\beta$ -quartz)<sup>3,4</sup> restricts its area of applications. This is the reason why considerable efforts have been devoted to find analogous materials with better intrinsic properties. In this research, the 32-point group has been intensively investigated. For example, in contrast to  $\alpha$ -quartz where all tetrahedra are identical,  $M^{III}X^VO_4$  (M = B, Ga, Al, Fe and X = P, As) are described as a helical chain of  $M^{III}O_4$  and  $X^VO_4$  tetrahedra alternatively linked along the c-axis<sup>5–12</sup>. Most of these homeotypes present a higher electromechanical coupling than  $\alpha$ -quartz and can reach up to  $^{10,13}$   $k_{26} \sim 22\%$  in GaAsO<sub>4</sub> without undergoing any phase transition until its decomposition temperature (1303 K)<sup>9,14</sup>. Langatate or langasite are compounds with the A<sub>3</sub>BC<sub>3</sub>D<sub>2</sub>O<sub>14</sub> general formula and adopt to the P321 space group<sup>15</sup>. They can be described as a framework formed by five tetrahedra (three CO<sub>4</sub> and two DO<sub>4</sub>), one BO<sub>6</sub> octahedron, and A is a decahedral site coordinated by eight oxygen atoms. In particular, the La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> langasite has a piezoelectric-strain constant  $(d_{11} \sim -6.5 \text{ pC/N})^{16}$ 2.5 times higher than in  $\alpha$ -quartz, an electromechanical coupling coefficient of  $k_{26} = 13.4\%^{17}$  and no structural phase transition between room temperature and its melting point at 1470°C<sup>18</sup>. More recently, first-principles-based calculations predicted in BaZnO<sub>2</sub> a piezoelectric-strain constant and an electromechanical coupling coefficient of <sup>19</sup>:  $d_{11} = 11.84$  pC/N and  $k_{11} = 35.7\%$ . This compound shares the same space group as  $\alpha$ -quartz. However, the screw axis of this trigonal unit cell is defined by the arrangement of corner-sharing ZnO<sub>4</sub> tetrahedra around the barium atom, which is located in a distorted 8-fold oxygen atom coordination<sup>20</sup>.

In this context, we are interested in the NaLn(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O family, with Ln = La–Yb, as promising piezoelectric materials. The crystal structure of the compounds within this family have been reported in the literature at room temperature<sup>21–29</sup>. All structures belong to the P3<sub>1</sub>21 space group or in its enantiomorphic analog P3<sub>2</sub>21. The structure consists of LaO<sub>9</sub> tricapped trigonal prisms, NaO<sub>8</sub> square-antiprisms and SO<sub>4</sub> tetrahedra polyhedra. The structural water is helically placed along the 3<sub>1</sub> axis<sup>24,26</sup>. To our knowledge, there is no experimental or theoretical study of the piezoelectric properties devoted to this family. Our study naturally began with the simpliest compound within this family, NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, since it is the only one that does not have magnetic properties. However, the calculation of its piezoelectric properties was not possible because of unstable phonon modes at the zone-center.

In this article, we report the existence and the mechanism in  $NaLa(SO_4)_2$ .H<sub>2</sub>O of a displacive phase transition at 200 K from

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<sup>†</sup> Electronic Supplementary Information (ESI) available. See DOI: 00.0000/00000000.

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Physical Chemistry Chemical Physics Accepted Man

the nonpolar P3<sub>1</sub>21 to the polar P3<sub>1</sub> space groups. The discussion of this article is organized in four parts. The first part discusses the structure and the lattice dynamics of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O in the P3121 space group. Although our calculation reproduced quite well the experimental infrared spectrum, they revealed three unstable polar phonons suggesting a displacive phase transition at low temperature toward a P31 subgroup. The used methodology to identify the polar P31 space group and the mechanism of the P3<sub>1</sub>21-P3<sub>1</sub> phase transtion is explained from symmetry-adapted distortion modes in the second part. This approach involves describing the P3<sub>1</sub> structure as arising from the P3<sub>1</sub>21 structure with one (or more) static symmetry-breaking structural distortion(s). The third part is purely experimental and confirms, independently with respect to our calculations, the DFT predictions. We determined the temperature where the phase transition takes place by infrared spectroscopy and x-ray diffraction performed below this temperature on single crystal identified the P31 space group. The last part is devoted to the piezoelectric properties of this new P31 phase.

#### 2 Synthesis and Experimental setup

The synthesis and the crystal growth process of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O have already been detailed in ref.<sup>30</sup>. A suitable single crystal  $(202 \times 201 \times 150 \ \mu m)$  was mounted on a cryoloop and the crystal structure was determined by x-ray diffraction using a Bruker 4-circle D8 Venture diffractometer with a PHOTON II area detector, using Mo K<sub> $\alpha$ </sub> radiation (0.71073 Å) from an Incoatec I $\mu$ S 3.0 microsource with focusing mirrors operating at 50 kV and 1 mA. The data collection was performed at 100 K using APEX4 sofware and the structure was solved by direct methods. A first determination of the structure by using SHELXT 2018/2 sofware led to a bad solution with R1 = 13.7%. By introducing an inversion twin law defined by the (0 1 0, 1 0 0, 0 0 -1) matrix, the refinement by using SHELXL 2019/1 software resulted in a good structural model (R1 = 1.5%) with the P3<sub>1</sub> space group. The absorption correction type is multi-scan performed by SADABS-2016/2 - Bruker AXS area detector scaling.

Infrared measurements were carried out in the far-infrared  $(50-600 \text{ cm}^{-1})$  and mid-infrared  $(600-4000 \text{ cm}^{-1})$  regions. We used a Bruker IFS 66V Fourier transform spectrometer using a black body source and two different beamsplitters covered the whole spectral region: bromide potassium (mid-infrared) and Ge-coated (far-infrared). A Si-bolometer detector cooled at 4 K was used to probe the far-infrared domain with extra sensitivity and a N<sub>2</sub>-cooled MCT (mercury cadmium telluride) detector was used in the mid-infrared domain. The spectral resolution was 2 cm<sup>-1</sup> and 64 scans were accumulated for each spectrum. The measurements were performed in the 25–295 K range using a cold finger helium cryostat. The sample was gently ground with polyethylene (resp. bromide potassium) powder according to the 1/70 (resp. 1/300) mass ratio and compressed under 8 tons to form an isotropic pellet of 12 mm diameter.

#### 3 Computational details

Calculations were performed within the density functional theory (DFT) and using a plane-wave pseudopotentials method as im-



Fig. 1 (a) Relaxed crystal structure of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O in the P3<sub>1</sub>21 space group along the *a*-axis. This representation highlights the three different polyhedra. The polyhedra centered on Na-, La- and S-atoms are displayed in cyan, green and yellow, respectively. The oxygen and hydrogen atoms are in red and white balls, respectively. (b) Schema of the bifurcated hydrogen bonding in the structure.

plemented in the ABINIT package<sup>31</sup>. The exchange-correlation energy functional is evaluated using the generalized gradient approximation (GGA) parametrized by Perdew, Burke and Ernzerhof (PBE)<sup>32</sup>. The all-electron potentials are replaced by normconserving pseudopotentials generated according to the Troullier-Martins scheme. Na $(2s^2, 2p^6, 3s^1)$ , La $(5s^2, 5p^6, 5d^1, 6s^2)$ , S $(3s^2, 5p^6, 5d^1, 6s^2)$ , S}, S $(3s^2, 5p^6, 5d^1, 6s^2)$ , S}, S}, S}, S}  $3p^4$ ), O(2s<sup>2</sup>, 2p<sup>4</sup>) and H(1s<sup>1</sup>)-electrons are considered as valence states. The electronic wave functions are expanded in plane-waves up to a kinetic energy cutoff of 67 Ha and integrals over the Brillouin zone are approximated by sums over a  $6 \times 6 \times 6$  mesh of special k-points according to the Monkhorst-Pack scheme  $^{33}$ . These *k*-point sampling and kinetic energy cutoff give converged results. Lattice parameters and atomic positions were fully relaxed using a Broyden-Fletcher-Goldfarb-Shanno algorithm until the maximum stresses and residual forces were less than  $7 \times 10^{-4}$  GPa and  $6 \times 10^{-6}$  Ha/Bohr, respectively. Dynamical matrix at the zone center, Born effective charges, dielectric, elastic and piezoelectric tensors have been calculated within a variational approach to density functional perturbation theory. Infrared absorbance spectra were calculated according to the formalism described in ref.  $^{34}$ . In our calculations, the Cartesian x (resp. z) axes are collinear to the a (resp. c) crystal directions. The y-axis is the free axis.

#### 4 Results and discussion

#### 4.1 Structure and lattice dynamics of the P3<sub>1</sub>21 phase

In 1994, Blackburn *et al.*<sup>26</sup> reported for the first time the crystal structure of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O at room temperature using X-ray diffraction. However, their sructure was not fully resolved as the position of the water molecules remained uncertain. In 2005, Perles *et al.*<sup>24</sup> located the hydrogen atoms from the water molecule using a difference Fourier analysis and included them in the refinement process. In agreement with Blackburn *et al.*<sup>26</sup>, they reported that NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O crystallizes at room temperature in

the acentric trigonal system with the  $P3_121$  ( $D_3^4$ ) space group and the lattice parameters a = 7.0538(5) and c = 12.9625(14) Å. The asymmetric unit contains 9 atoms (see Table 1). All atoms occupy the general 6c Wyckoff position with  $C_1$  site symmetry except lanthanum (3a), sodium (3b) and water oxygen (3a) atoms which occupy special Wyckoff positions with  $C_2$  site symmetry.

Recently, the crystal structure of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O has also been investigated by our group using x-ray diffraction to understand the dehydration process at high temperature<sup>30</sup>. Similarly with this study, the consideration of hydrogen atoms in the structural model does not improve our refinement. Results of our refinement, reported in Table 1 at room temperature, are consistent with those of Perles et al.<sup>24</sup> as shown by the small lattice distortion ( $\eta = 0.02\%$ ) and similarity factor<sup>35</sup> ( $\Delta = 0.2\%$ )<sup>36</sup> calculated without hydrogen atoms. The higher discrepancy between the two experimental structure listed in Table 1 is observed for the water oxygen atom  $(O_{5w})$  with an atomic displacement of (-0.0055, -0.0055, 0.0000) in reduced units. In the structure proposed by Perles *et al.*<sup>24</sup>, the position of the  $O_{5w}$  and hydrogen atoms are not very accurate considering their high standard deviation values. In our refinement, the position of the atoms are well determined with a smaller standard deviation. This is the reason why this structure was used as starting point in our DFT-based calculations.

All the studies report that the NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O structure at room temperature can be seen as built from LaO<sub>9</sub> tricapped trigonal prisms, NaO<sub>8</sub> square-antiprisms and SO<sub>4</sub> tetrahedra polyhedra (Figure 1(a)). The lanthanum is coordinated with six sulfate groups and one water molecule. Over the six sulfate groups, two share their edges by two oxygen atoms and the other four share their corners by one oxygen atom. Sodium is coordinated by six sulfate groups (four are corner-sharing and two are edgesharing). Sulfur atoms are in a slightly irregular tetrahedron environment. The water molecules are helicaly placed along the 3<sub>1</sub> axis. Each hydrogen atom form a bifurcated hydrogen bond with a sulphate oxygen atom: H...O<sub>2</sub> and H...O<sub>3</sub> (see Figure 1(b)).

Relaxation of the NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O structure has been performed by DFT and results are listed in Table 1. We observe a dilatation of the calculated unit cell about 1.4% along the three directions, leading to a calculated volume 4.2% higher than in the experiments. These trends and these relative errors are commonly observed with the PBE functional. The calculated atomic positions show similar agreement with respect to the two sets of experimental data. The similitude factor between our calculation and the atomic positions from Perles *et al.*<sup>24</sup> is  $\Delta = 0.015$  including hydrogen atoms. Without the hydrogens in the calculation of  $\Delta$ , we get  $\Delta = 0.010$  with the structure from Perles *et al.* and  $\Delta = 0.009$  with the structure from Azeroual *et al.*. The calculated average of the La-O, Na-O and S-O distances are slightly overestimated between 1.0 and 1.6% in comparison with the experimental ones. The calculated position of the water oxygen  $(O_{5w})$  is in excellent agreement with the experimental refinement from Azeroual et al. and shows a difference of (-0.0018, -0.0018, 0.0000) in reduced units against (-0.0073, -0.0073, 0.0000) for the O<sub>5w</sub> position refined by Perles et al.. The calculated position of hydrogen atoms gives the higher difference between our calculation and

			20			
		Experiment <sup>24</sup>	Experiment <sup>30</sup>	Calculation		
		[300 K]	[300 K]	[0 K]		
T - //						
			70516(1)	7 1 4 7 0		
		/.0538(5)	/.0516(1)	/.14/0		
		12.9625(14)	12.9587(2)	13.1405		
c/a	2	1.8377	1.8377	1.8403		
Ω <sub>0</sub> [A	.2]	558.55	558.042(18)	581.295		
Atomic positions (reduced units)						
La	x x	0.5674(1)	0.5674(1)	0.5643		
Ца	v	0.5674(1)	0.5674(1)	0.5643		
	, 7	0.0000	0.0000	0.0000		
0,	v	0.0000	0.4969(1)	0.0000		
01	A V	0.4930(9)	0.7909(1) 0.3635(1)	0.3583		
	y 7	0.3030(9)	0.3033(1) 0.8254(1)	0.3303		
0.	Z	0.6237(3)	0.6234(1) 0.6102(2)	0.62/3		
$O_2$	X	0.0109(7)	0.0103(2)	0.0040		
	У	0.7400(7)	0.7396(1)	0.7339		
0	z	0.8184(3)	0.8182(8)	0.8210		
$O_3$	X	0.4090(8)	0.4085(2)	0.4101		
	У	0.163/(8)	0.162/(2)	0.1621		
0	Z	0.0262(4)	0.0260(1)	0.0297		
$O_4$	х	0.49/5(9)	0.498/(2)	0.5028		
	У	0.8821(9)	0.8815(2)	0.8832		
	Z	0.0137(3)	0.0135(1)	0.0155		
S	х	0.5600(3)	0.5599(1)	0.5556		
	у	0.5474(3)	0.5473(1)	0.5425		
	Z	0.7533(1)	0.7533(1)	0.7559		
$O_{5w}$	х	0.9302(14)	0.9247(3)	0.9229		
	У	0.9302(14)	0.9247(3)	0.9229		
	Z	0.0000	0.0000	0.0000		
Na	х	0.0000	0.0000	0.0000		
	у	0.4700(6)	0.4693(1)	0.4784		
	Z	1/6	1/6	1/6		
Н	х	0.049(17)	-	0.0589		
	у	0.93(2)	-	0.9523		
	Z	0.056(7)	-	0.0303		
Volum		noluhodro D[V]	33			
VOIUN	ie or j	polylieura P[A] (A	1)	20 441		
P[Na]		28.050	28.014	29.441		
P[La]		32.937	32./3/	33./53		
P[S]		1.643	1.641	1.701		
Mean	dista	nces (Å)				
<na-< td=""><td>0&gt;</td><td>2.590</td><td>2.589</td><td>2.633</td></na-<>	0>	2.590	2.589	2.633		
<la-(< td=""><td>)&gt;</td><td>2 553</td><td>2.547</td><td>2 570</td></la-(<>	)>	2 553	2.547	2 570		
<s-0< td=""><td>&gt;</td><td>1.475</td><td>1.474</td><td>1.492</td></s-0<>	>	1.475	1.474	1.492		
		0				
Hydro	ogen l	oond distances (Å	): $O_{5w} - H \cdots O$			
$O_{5w}$	. O <sub>2</sub>	3.228(5)	3.240(16)	3.442		
$O_{5w}$	. O <sub>3</sub>	2.945(9)	2.974(3)	3.041		
Н (	$D_2$	2.1(1)	-	2.460		
Н (	D <sub>3</sub>	2.3(1)	-	2.188		

Table 1 Structural parameters in the P3<sub>1</sub>21 phase of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. P(X) is the polyhedra centered on the X-atom.



Fig. 2 Experimental infrared absorbance spectrum of NaLa(SO<sub>4</sub>)<sub>2</sub>. H<sub>2</sub>O in the P3<sub>1</sub>21 phase (295 K) and the corresponding calculated spectrum (0 K). The calculated spectrum is displayed using a Lorentzian line shape and a constant linewidth fixed at 2 cm<sup>-1</sup>.

the experiment where a difference of (0.0099, 0.0223, -0.0257) in reduced unit can be observed.

Group theory predicts that each of the six (resp. three) atoms of the NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O asymmetric unit located on the  $C_1$ -site (resp.  $C_2$ -site) contributes to:  $3A_1 \oplus 3A_2 \oplus 6E$  (resp.  $A_1 \oplus 2A_2 \oplus$ 3E). Thus, the corresponding irreducible representation of the acoustic ( $\Gamma_{acc}$ ) and optical ( $\Gamma_{opt}$ ) vibrational modes at the zonecenter ( $\Gamma$ -point) is:  $\Gamma_{acc} = A_2 \oplus E$  and  $\Gamma_{opt} = 21A_1 \oplus 23A_2 \oplus 44E$ . The *E* representation is simultaneously infrared and Raman active whereas the  $A_2$  (resp.  $A_1$ ) representation is only infrared (resp. Raman) active.

The experimental infrared spectrum measured at room temperature using an absorbance configuration is reported in Figure 2 within the 50-3800 cm<sup>-1</sup> range (see Figure S1 in ESI for the 1800–3000 cm<sup>-1</sup> range). This spectrum has been normalized on the band located at 595 cm<sup>-1</sup> which is common to the far- and mid-infrared domain. The DFT infrared spectrum calculated at 0 K is also reported in this figure. The band width cannot be calculated within the framework of the harmonic approximation and is arbitrarily fixed at 2 cm<sup>-1</sup>. The number of calculated bands, their frequency position and their relative intensity are in good agreement with the experiment. We just observe an inversion in the relative intensity of the triplet about 1100 cm<sup>-1</sup>. The slight underestimation (except for the couple of bands around 3600 cm<sup>-1</sup>) in the calculated frequencies could be related to the difference of temperature between the calculation and the experiment.

Mode assignments (given following Herzberg's notation <sup>37</sup>) are carried out from the analysis of the eigendisplacement vectors obtained by diagonalization of the dynamical matrix. The experimental spectrum can be divided into three regions. The first region ( $3800-1500 \text{ cm}^{-1}$ ) is dominated by motions of the water molecules. The bands centered at 3558 and 3508 cm<sup>-1</sup> are assigned to the O-H asymmetric ( $v_3$ ) and symmetric ( $v_1$ ) stretching



Fig. 3 Eigendisplacement vector of the three unstable modes in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O with the P3<sub>1</sub>21 space group. The color code is the same than in Figure 1. The frequency in cm<sup>-1</sup> is between brackets.

vibrations. The band at 1619 cm<sup>-1</sup> is ascribed to the H-O-H bending deformation  $(v_2)$ . The shape and the position of the stretching bands show that water molecules have the same environment and form hydrogen bonds of weak intensity. Thus, we have one type of water molecules which is consistent with the chemical formula. Combination bands of sulfate groups can also be observed within this domain (see Figure S1 in ESI). The second region (1500-400 cm<sup>-1</sup>) is dominated by the motions of sulphate groups. The intense triplet of bands about 1132 cm<sup>-1</sup> dominates the infrared spectrum and corresponds to the stretching modes. The bands at 1150 and 1130 cm<sup>-1</sup> are assigned to asymmetric stretching  $(v_3)$ while the remaining one is the symmetric stretching  $(v_1)$ . The bending modes of sulphate groups are observed between 600 and  $400 \text{ cm}^{-1}$  and bands have medium intensity. The couple of bands around 620 cm<sup>-1</sup> are assigned to antisymmetric bending vibrations ( $v_4$ ) whereas the one around 460 cm<sup>-1</sup> is the symmetric bendings ( $v_2$ ). The last region (400–50 cm<sup>-1</sup>) is complex to analyze because this is the domain where external vibrations of water, sulfate and LaO<sub>9</sub> appears. This region is dominated by an intense band at 206 cm<sup>-1</sup> assigned to deformations of water molecules combined with deformation of NaO<sub>8</sub> and LaO<sub>9</sub> polyhedra. The remaining bands have low intensity. The band about  $305 \text{ cm}^{-1}$  is a wagging of water molecules. The libration of sulphate groups are evidenced about  $110 \text{ cm}^{-1}$ .

Below 50 cm<sup>-1</sup>, our calulations reveal two distinct unstable zone-center modes, suggesting that NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O undergoes a displacive phase transition at low temperature to a subgroup of the P3<sub>1</sub>21 space group. The mode with the largest imaginary frequency (123*i* cm<sup>-1</sup>) belongs to the A<sub>2</sub> irreducible representation whereas the other mode belongs to the E representation and has an imaginary frequency at 97*i* cm<sup>-1</sup>. The eigendisplacement vectors of these three modes correspond to a twisting of water molecules (Figure 3). From symmetry considerations, the number of potential subgroups can only be three and are: trigonal P3<sub>1</sub>, monoclinic C2 or triclinic P1. Indeed, the P3<sub>1</sub> phase can be obtained from the condensation of the A<sub>2</sub> unstable mode in the P3<sub>1</sub>21 phase whereas the C2 or P1 phase can be obtained from the condensation of the unstable E mode in the P3<sub>1</sub>21 phase. In the

(c)



Fig. 4 (a) Relaxed crystal structure of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O in the P3<sub>1</sub> space group along the *a*-axis. (b) Schema of the hydrogen bonding in the structure. The same color code than in Figure 1 is used.

Fig. 5 Distortion vector between the P3<sub>1</sub> and the P3<sub>1</sub>21 phases in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. This vector has been calculated from the DFT structures (a), the DFT structures whithout hydrogen atoms (b) and our experimental structures for which hydrogen atoms could not be determined by x-ray diffraction (c). The Na-, La-, S- and O-atoms are displayed in cyan, green, yellow and red, respectively.

case of the condensation of the E-mode, we have two possibilities because this representation is twofold degenerate. In contrast to the the parent  $P3_121$  group, these three subgroups belong to pyroelectric groups. In addition, the unit cell of these low symmetry structures is not enlarged with respect to the parent structure ( $P3_121$  phase) as the instabilities are at the zone center. Only the number of atoms in the asymmetric unit can change between these structures.

#### 4.2 Prediction of the P3<sub>1</sub>21-P3<sub>1</sub> phase transition and mechanism

Identification. The relaxed lattice parameters of the P3<sub>1</sub>, C2 and P1 phases are listed in Table 2 with their electronic energy relative to the P3<sub>1</sub>21 phase. As expected, these three phases are more stable than the P3<sub>1</sub>21 phase and their primitive unit cell volume  $(\Omega_0 = 574-577 \text{ Å}^3)$  is very similar to that calculated for the P3<sub>1</sub>21 phase  $(\Omega_0 \sim 581 \text{ Å}^3)$ . The energy of the C2 and the P3<sub>1</sub>21 phases differ by -25.04 meV. The P1 phase is more stable than the C2 phase by about the same amount of energy. The lowest energy configuration corresponds to the trigonal P3<sub>1</sub> phase with a decrease of 113 meV (resp. 87.9 meV) with respect to the P3<sub>1</sub>21 (resp. C<sub>2</sub>) phase. We checked that this tendency should be preserved even under small variation of the unit cell volume. Further phonon calculations at the zone-center do not reveal any unstable mode, identifying this P3<sub>1</sub> phase as potential ground state at low temperature.

The structure of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O in the P3<sub>1</sub> phase (Table 2) is similar to that in the P3<sub>1</sub>21 phase (Table 1). The lattice parameters are slightly smaller (-0.5% for *a* and -0.2% for *c*), yielding an underestimation of -1.2% for the unit cell volume. The *c*/*a* ratio is preserved during the phase transition. The coordination of the lanthanum (9), sodium (8) and sulfur (4) with oxygen atoms remain unchanged (Figure 4a). The water molecules are also along the 3<sub>1</sub> screw axis with the water oxygen atom (O<sub>5w</sub>) coordinated to the lanthanum. However, the loss of the twofold symmetry leads each atoms at the 6*c* Wyckoff positions in the P3<sub>1</sub>21 phase to split into two in the P3<sub>1</sub> phase. Thus, the sulphur atoms can be separated into types  $S_1$  and  $S_{1'}$  in the P3<sub>1</sub> phase which form two slightly different sulphate units. The four inequivalent oxygen atoms bonded to  $S_1$  (resp.  $S_{1'}$ ) are labeled as  $O_1$ ,  $O_2$ ,  $O_3$  and  $O_4$ (resp.  $O_{1'}$ ,  $O_{2'}$ ,  $O_{3'}$  and  $O_{4'}$ ). The La-O, Na-O and S-O intrapolyhedral mean distances do not evolve with respect to the P3<sub>1</sub>21 phase. A similar observation can be made on the volume of the polyhedra. In contrast, we observe that the hydrogen bonding is strengthened in the P31 phase as the different O...H and O<sub>5w</sub>...O distances are significantly shorter (Tables 1 and 3): the calculated O...H (resp. O<sub>5w</sub>...O) distances are  $\sim 2.0$  Å (resp. 2.9–3.0 Å) in the P3<sub>1</sub> phase against 2.2–2.5 Å (resp. 3.0–3.4 Å) in the P3<sub>1</sub>21 phase. However, the hydrogen bond is no longer bifurcated in the P3<sub>1</sub> phase as the  $H_1$ -O<sub>3'</sub>,  $H_1$ -O<sub>2</sub> and  $H_{1'}$ -O<sub>3</sub> interatomic distances range between 2.563 and 2.857 Å. Thus, all these structural results suggest that the increase in the strength of the hydrogen bond would be responsible for the volume decrease during the phase transition.

**Mechanism.** We can quantitatively estimate the atoms involved in the transition from the knowledge of the structural distortion vector,  $\boldsymbol{\tau}$ . This vector is the symmetry-breaking structural distortion of the P3<sub>1</sub>21 phase that leads to the P3<sub>1</sub> phase and can be defined as:

$$\tau_{\alpha\kappa} = r_{\alpha}(\kappa) - r_{\alpha}^{0}(\kappa), \qquad (1)$$

where  $\mathbf{r}(\kappa)$  and  $\mathbf{r}^{0}(\kappa)$  are respectively the position of the  $\kappa^{th}$  atom in the P3<sub>1</sub> phase and the corresponding one in the P3<sub>1</sub>21 phase expressed in the setting of the low-symmetry space group. As the origin is undefined in a polar structure, we considered the center of mass of the unit cell as invariant during the transition. This condition represents a shift along the z-direction of 0.0046 in reduced unit of the atomic positions in the P3<sub>1</sub> phase. The structural distortion vector is listed in Table 4 and displayed in Figure 5(a). The amplitude of this distortion is defined by the modulus of  $\tau$ :

$$T = |\boldsymbol{\tau}| = Z \sum_{\alpha,\kappa} \tau_{\alpha\kappa}^2, \tag{2}$$

Sym.	Freq.	Space	Lattice parameters and angles	Volume	$\Delta E$
	$[cm^{-1}]$	group		[Å <sup>3</sup> ]	[meV]
A <sub>2</sub>	123 <i>i</i>	P31	a = 7.111 Å, $b = 7.111$ Å, $c = 13.109$ Å	574.116	-112.98
			$lpha=90.00^\circ,eta=90.00^\circ,\gamma=120.00^\circ$		
Е	97 <i>i</i>	C2	a = 7.126 Å, $b = 7.142$ Å, $c = 13.127$ Å,	578.952	-25.04
			$lpha = 89.34^{\circ},  eta = 90.00^{\circ},  \gamma = 119.93^{\circ}$		
E	97 <i>i</i>	P1	a = 7.125 Å, $b = 7.126$ Å, $c = 13.119$ Å,	576.960	-55.34
			$lpha = 90.32^{\circ},  eta = 89.26^{\circ},  \gamma = 119.97^{\circ}$		

Table 2 Relaxed lattice parameters, including unit cell volume, and calculated energies  $\Delta E$  (relative to the P3<sub>1</sub>21 phase and per unit cell) of the different structures obtained from the condensation of each unstable phonon modes in the P3<sub>1</sub>21 phase. The symmetry and frequency of the listed mode is for the P3<sub>1</sub>21 phase.

		Calc.	Exp.			Calc.	Exp.	
Lattice parameters								
a (Å)		7.111	7.023(1)	c/a		1.843	1.843	
b (Å)		13.109	12.945(1)	$\dot{\Omega}_0$ (Å	<sup>3</sup> )	574.11	552.89(10)	
Atom	ic pos	itions (red	uced units)					
La	х	0.5787	0.5768(1)	$H_1$	х	0.0814		
	У	0.5659	0.5636(1)		У	0.9889		
	Z	0.0056	0.0068(1)		Z	0.0024		
$O_1$	х	0.5180	0.5154(2)	$S_{1'}$	х	0.5535	0.5554(1)	
	У	0.3660	0.3651(2)		У	0.5716	0.5711(1)	
	Z	0.8329	0.8324(1)	~ /	Z	0.2515	0.2538(1)	
$O_2$	х	0.5898	0.5916(2)	$O'_1$	х	0.3700	0.3689(2)	
	у	0.7310	0.7329(2)		У	0.4865	0.4889(2)	
0	Z	0.8271	0.8254(1)	0	Z	0.1774	0.1807(1)	
$O_3$	х	0.3916	0.3956(2)	$O_{2'}$	х	0.7552	0.7544(2)	
	У	0.1436	0.1461(2)		У	0.6411	0.6349(2)	
0	z	0.0303	0.028/(1)	0	z	0.1887	0.1893(1)	
$O_4$	X	0.5213	0.5201(2)	$O_{3'}$	x	0.1850	0.1800(2)	
	у	0.0094	0.00/5(2)		у	0.4243	0.4156(2) 0.0776(1)	
C.	Z	0.0240	0.0240(1)	0.'	Z	0.9/33	0.9770(1)	
51	X	0.5555	0.3347(1) 0.5447(1)	04	X	0.0793	0.8760(1)	
	у	0.3430	0.3447(1) 0.7601(1)		у	0.4702	0.4704(1)	
0-	v	0.0342	0.7001(1) 0.0344(3)	н.,	v	0.9939	0.7700(1)	
05w	v	0.9342	0.9344(3) 0.9148(3)	11]/	v	0.7242		
	у 7	0.9746	0.9763(1)		y 7	0.0210		
Na	x	0.0065	0.0058(1)		2	0.7521		
Itu	v	0.4741	0.4708(1)					
	Z	0.1740	0.1750(1)					
Volun	ne of	polyhedra	P[X] (Å <sup>3</sup> )					
P[Na]		29.017	27.588	P[La]		33.641	32.567	
$P[S_1]$		1.702	1.649	$P[S_{1'}]$	]	1.700	1.650	
		0						
Mean	Mean distances (Å)							
Na-O		2.632	2.585	La-O		2.572	2.547	
$S_1-O$		1.492	1.477	S <sub>1′</sub> -O		1.492	1.477	
T Trada								
nyuro		2 9 971	2, 95, 95, 95, 100, 100, 100, 100, 100, 100, 100, 10	- п···		2.064	2074(1)	
$O_{5w}$	$O_{5w} \cdots O_2 = 2.871 = 2.858(1)$		$O_{5w}$	$0_{2'}$	2.90 <del>4</del> 2.101	2.7/4(1) 3.047(1)		
$U_{5w} \cdots U_3$ 2.910 2.86 H $Q_2$ 1.045		2.000(1)	U <sub>5w</sub>	0	1 000	3.04/(1)		
$H_{11} = 0.3 = 1.940$ $H_{11} = 0.7 = 1.990$								
<u> </u>	$0_{2'}$	1.990						

Table 3 Calulated (0 K) and experimental (100 K) structural parameters in the P3<sub>1</sub> phase of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. The experimental structure at 100 K is deposited at the Cambridge crystallographic data centre with deposition number: ICSD 2207042.

where *Z* is the number of formula units (*Z* =3). We found the the P3<sub>1</sub>21-P3<sub>1</sub> transition is accompanied by a distortion whose the amplitude is: T = 1.72 Å. In particular, the hydrogen atoms and the atoms labelled O<sub>5w</sub> contribute by 60% [=  $ZA_{H_1}^2/T^2 + ZA_{H_{1'}}^2/T^2$ ] and 17% [=  $ZA_{O_{5w}}^2/T^2$ ] to this distortion, respectively. The third main contribution is observed for O<sub>2'</sub>-atoms and drops to about 6% only. The contribution of all other atoms remain below 4% each, but represent 17% of the overall distortion. The participation of the sulfur atom labelled S<sub>1</sub> is almost zero. Thus, the structural water and the O<sub>2'</sub>...H hydrogen bonds should drive the P3<sub>1</sub>21–P3<sub>1</sub> transition by ~83%.

The phonons involved in the phase transiton can also be identified from the structural distortion vector. Indeed, the set of phonon eigenvectors obtained from the diagonalization of the dynamical matrix in the P3<sub>1</sub>21 phase,  $\{\mathbf{e}^{j}\}_{j=1,...,3\kappa}$ , define a complete basis as they satisfy the orthonormalization condition:  $\sum_{\alpha\kappa} e^{i}_{\alpha\kappa} e^{j}_{\alpha\kappa} = \delta_{ij}$  where *i* and *j* are phonon normal modes and  $\delta$  is the Kronecker symbol. Thus, the structural distortion vector can be decomposed into this basis according to:

$$\tau_{\alpha\kappa} = \sum_{j} Q_{j} e^{j}_{\alpha\kappa}, \tag{3}$$

and the mode amplitude  $Q_j$  is then given by:

$$Q_j = \sum_{\alpha\kappa} e^j_{\alpha\kappa} \tau_{\alpha\kappa}.$$
 (4)

It is also convient to introduce the cosine director,  $\Lambda_i$ , with respect to the distortion direction  $\mathbf{e}^{j}$ . Indeed, as by definition  $\sum_{i} \Lambda_{i}^{2} = 1$ , this quantity better describes the relative contributions of the different normal modes entering into the distortion. In this case,  $Q_i = T\Lambda_i$ , where T is the distortion amplitude discussed in the previous paragraph. Table 5 reports the dominant contributions  $(\Lambda_i > 0.01)$  of the normal modes from the P3<sub>1</sub>21 phase to the distortion vector. As expected, the unstable  $A_2$  mode at 123i has the highest contributions with a value of  $\Lambda = 0.694$ . However, the P3<sub>1</sub> phase does not arise from the condensation of this unstable mode only, but also requires the participation of six additional stable modes. Four modes calculated at 123i, 49, 79, 97 and 321 cm<sup>-1</sup> also belong to the A<sub>2</sub> irreducible representation and two modes at 60 and 87 cm<sup>-1</sup> belong to the A<sub>1</sub> irreducible representation. The contribution of the polar A2 modes to the distortion represents 85%. These modes are therefore the primary modes and drive

View Article Online DOI: 10.1039/D3CP00587A

Symmetry	Frequency [cm <sup>-1</sup> ]	$\Lambda_j$
A2	123 <i>i</i>	0.694
A <sub>2</sub>	49	0.549
A1	60	0.207
A <sub>2</sub>	79	-0.153
A1	87	0.299
A <sub>2</sub>	97	-0.160
A <sub>2</sub>	321	0.120

		$\tau_{\alpha\kappa}$		$A_{\kappa} =$
κ	$\alpha = x$	$\alpha = y$	$\alpha = z$	$[\sum_{lpha}  au_{lpha\kappa}^2]^{1/2}$
La	0.0972	0.0099	0.0141	0.099
	(0.0144)	(0.0016)	(0.0011)	
O1	0.1552	0.0475	0.0114	0.163
	(0.0255)	(0.0077)	(0.0009)	
O <sub>2</sub>	-0.0946	-0.0184	0.0204	0.099
	(-0.0147)	(-0.0030)	(0.0016)	
O <sub>3</sub>	-0.066	-0.1145	-0.0524	0.142
	(-0.0185)	(-0.0185)	(-0.0040)	
$O_4$	0.1097	0.0385	0.0634	0.132
	(0.0185)	(0.0062)	(0.0048)	
$S_1$	-0.0109	0.0151	0.0094	0.021
	(-0.0003)	(0.0024)	(0.0007)	
$O_{5w}$	0.1005	-0.0349	-0.3936	0.408
	(0.0112)	(-0.0056)	(-0.0300)	
Na	0.0621	-0.0268	0.0364	0.077
	(0.0065)	(-0.0043)	(0.0028)	
$H_1$	0.0304	0.2265	-0.4272	0.485
	(0.0226)	(0.0366)	(-0.0325)	
$S_{1'}$	0.0215	0.0992	0.0377	0.108
	(0.0110)	(0.0160)	(0.0029)	
$O_{1'}$	0.1053	-0.0370	0.0045	0.112
	(0.0117)	(-0.0060)	(0.0003)	
$O_{2'}$	0.0213	0.2260	0.0675	0.237
	(0.0212)	(0.0365)	(0.0051)	
O <sub>3′</sub>	0.11800	0.0874	0.0086	0.147
	(0.0236)	(0.0141)	(0.0007)	
$O_{4'}$	0.0678	-0.1649	0.0628	0.189
	(-0.0038)	(-0.0266)	(0.0048)	
$H_{1^{\prime}}$	-0.0787	-0.2109	-0.5534	0.598
	(-0.0281)	(-0.0341)	(-0.0421)	

Table 4 Calculated atomic structural distortion vector ( $\tau$ ) of the P3<sub>1</sub> phase with respect to the P3<sub>1</sub>21 phase in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. This distortion has been calculated considering the center of mass as invariant. Only atoms of the asymmetric unit are listed. All data are in Cartesian coordinates (Å) except the data between brackets which are in reduced units.  $A_{\kappa}$  is the partial atomic modulus satisfying  $T = Z \sum_{\kappa} A_{\kappa}^2$ .

Table 5 Contributions  $\Lambda_j$  (see text) of the phonon modes j to the distortion linking the P3<sub>1</sub>21 and the P3<sub>1</sub> structures in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. Only contributions higher than 0.01 are listed.

the transition. They are also responsible of the polar character of the transition. This polarization can be roughly estimated as:

$$P_{\alpha} = \frac{1}{\Omega_0} \sum_{\beta \kappa} Z^*_{\alpha \beta}(\kappa) \tau_{\beta \kappa}, \tag{5}$$

where  $Z^*$  is the Born effective charge tensor of atom  $\kappa$ . We found  $P_z = 1.3 \ \mu \text{C.cm}^{-2}$  using the Born effective charges of the P3<sub>1</sub>21 phase, which is quite small compared to standard ferroelectric material like BaTiO<sub>3</sub> (~  $26\mu$ .cm<sup>-2</sup>)<sup>38</sup>. The two modes belonging to the fully symmetric A<sub>1</sub> irreducible representation contribute by 13% to the distortion. These modes do not break the symmetry of the P3<sub>1</sub>21 phase but contribute to the distortion by symmetry (von Neumann principle). They are therefore qualified of secondary modes and are only induced by the presence of the primary A<sub>2</sub> modes. All modes with A<sub>2</sub> or A<sub>1</sub> symmetry, and other than those listed in table 5, represent an overall participation of 2% to the distortion.

The infrared spectroscopy should provide an experimental evidence of this nonpolar–polar P3<sub>1</sub>21–P3<sub>1</sub> phase transition.

#### 4.3 Independent experimental confirmation of the P3<sub>1</sub>21– P3<sub>1</sub> phase transition

The temperature dependence of the infrared responses in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O has been recorded between 25 and 295 K. Figures 6 and 7 display the far-infrared (50–580 cm<sup>-1</sup>) and the mid-infrared (580–3700 cm<sup>-1</sup>) spectral region, respectively. The domain between 1800 and 3000 cm<sup>-1</sup> has been relegated in Supplementary information (Figure S1) as is not relevant for the present discussion. This domain reports bands with weak intensities assigned to combination modes of sulphate groups.

The infrared modes within the 50–1800 cm<sup>-1</sup> range show a monotonous dependence with a quasi-harmonic behaviour between 295 and 200 K. From this temperature, we observe the appearance of additional several bands which are increasingly better resolved down to 25 K. They are centered at 25 K about 1150, 1086, 545, 523, 488, 470, 450, 235, 214, 185, 160, 137 and 76 cm<sup>-1</sup>. The appearance of these bands highlights that NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O undergoes a phase transition at 200 K from the nonpolar P3<sub>1</sub>21 space group to a polar space group. X-ray diffraction has been performed at 100 K on a single crystal to identify this polar space group. Our refinement showed that the group in question was indeed the one predicted by our DFT calculations,



Fig. 6 Temperature dependence of the far-infrared modes in NaLa(SO<sub>4</sub>)<sub>2</sub>. H<sub>2</sub>O recorded between 295 and 25 K.



Fig. 7 Temperature dependence of the mid-infrared modes in  $NaLa(SO_4)_2.H_2O$  recorded between 295 and 25 K.

namely the P3<sub>1</sub> space group. Details of the data collection are summarized in Table S1 (ESI). This observed phase transition was found to be reversible by infrared spectroscopy and x-ray diffraction.

By reducing the symmetry of the P3<sub>1</sub>21 phase, the number of irreducible representations is also reduced. The correlation table between the D<sub>3</sub> and C<sub>3</sub> point group shows that the A<sub>1</sub> and A<sub>2</sub> irreducible representations in the P3<sub>1</sub>21 phase turn to be an unique *A* representation in the P3<sub>1</sub> phase. This *A*-representation is now both infrared and Raman active. Thus, the origin of the infrared additional bands previously discussed is correlated to the Raman  $A_1$ -modes in the P3<sub>1</sub>21 phase which are now active with *A*-symmetry in the P3<sub>1</sub> phase.

The calculated infrared spectra of the P3<sub>1</sub> phases is displayed in Figure 8. The irreducible representation of the optical phonon modes can easily be derived from the P3<sub>1</sub>21 phase as:  $\Gamma_{opt} =$  $44A \oplus 44E$ . Each atom of the asymmetric unit contributes by  $3A \oplus$ 3E. The infrared spectra are dominated within the 3200–3700 cm<sup>-1</sup> range by a doublet located about 3528 cm<sup>-1</sup> at room temperature. This doublet is assigned to the O-H stretching modes and undergoes a strong softening in frequency (~45 cm<sup>-1</sup>) with decreasing the temperature. This redshift is the fingerprint of interatomic O...H hydrogen bonds as a decrease in the intramolecular O-H force constants is expected when the intermolecular O...H hydrogen bonds are subjected to low temperature<sup>39</sup>. This suggests a reinforcement of the hydrogen bonds in the P3<sub>1</sub> phase in agreement with our DFT prediction.

Structural parameters of the phase solved in the P31 space group by x-ray diffraction are listed in Table 3 and compared with the ones from the DFT calculation. Data collection and refinement details are given in supporting information (Tables S1 to S5). The relative error is about +1.3% in the lattice parameters for each direction. The calculated c/a ratio is in perfect agreement with the experiment. The experiment shows that the unit cell volume in the P31 phase is slightly smaller (-0.9%) than in the P3<sub>1</sub>21 phase in agreement with the DFT results. This small difference is coherent with a phase transition at the Brillouin zone center. Although the experimental position of hydrogen atoms could not be determined, we can still get a distortion vector from the experimental positions between the P31 and the P3121 structures according to Eq. (1). We get an experimental distortion amplitude of  $T^{exp} = 0.96$  Å without the consideration of hydrogen atoms. This value is in good agreement with the calculated distortion amplitude ( $T^{calc} = 1.08$  Å) without hydrogen atoms (against  $T^{calc} = 1.72$  Å including hydrogen atoms). The experimental distortion vector (Figure 5(c)) agrees well with the DFT calculations (Figure 5(b)), which indicates that the experimental and the calculated P31 structures are very close. The water oxygen atoms  $(O_{5w})$  dominate the distortion.

#### 4.4 Piezoelectric properties of the P31 phase

This section is purely theoretical as piezoelectric measurements were not possible due to the small size of our single crystals.

In the  $C_3$ -point group, the piezoelectric-stress tensor has six independent nonzero elements<sup>40</sup>, namely  $e_{11}$ ,  $e_{12}$ ,  $e_{13}$ ,  $e_{33}$ ,  $e_{41}$  and



Fig. 8 Experimental infrared absorbance spectrum of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O in the P3<sub>1</sub> phase (25 K) and the corresponding calculated spectrum (0 K). The calculated spectrum is displayed using a Lorentzian line shape and a constant linewidth fixed at 2 cm<sup>-1</sup>.

	11	12	13	33	41	51
Piezo	electric-s	tress (C/r	n <sup>2</sup> )			
$e_{j\alpha}^{el}$	-0.024	-0.004	0.014	-0.013	0.016	0.015
$e_{j\alpha}^{ph}$	0.075	-0.135	-0.141	-0.113	-0.077	-0.052
$e_{j\alpha}$	0.051	-0.139	-0.127	-0.126	-0.061	-0.037
Diore	oloctric	train (nC	(NI)			
Plezo	Delectric-S	train (pC/	IN)			
$d_{j\alpha}$	1.40	-3.25	-0.98	-0.83	-3.42	-1.16

Table 6 Calculated independent elements of the piezoelectric-stress and piezoelectric-strain tensors in the P3<sub>1</sub> phase of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. The piezoelectric-stress ( $e = e^{el} + e^{ph}$ ) has been decomposed into an electronic ( $e^{el}$ ) and a vibrational ( $e^{ph}$ ) contribution. By symmetry with have the following relations:  $e_{11} = -e_{12} = -e_{62}$ ,  $e_{12} = -e_{22} = e_{61}$ ,  $e_{41} = -e_{52}$ ,  $e_{51} = e_{42}$  and  $e_{13} = e_{23}$ .

 $e_{51}$ . They have been calculated in the zero Kelvin limit and are listed in Table 6. We observe that the absolute values of  $e_{11}$ ,  $e_{41}$  and  $e_{51}$  are between 0.037 and 0.061 C/m<sup>2</sup>, which is similar to the values measured for  $e_{41}$  in  $\alpha$ -quartz<sup>2,41</sup> (0.04-0.06 C/m<sup>2</sup>). The highest piezoelectric-stress values are observed for the  $e_{12}$ ,  $e_{13}$  and  $e_{33}$  elements. Their absolute values are very close and reach 0.139 C/m<sup>2</sup> for  $e_{12}$ . This value is similar to that observed in  $\alpha$ -quartz<sup>2</sup> ( $e_{11} \sim 0.14$ -0.17 C/m<sup>2</sup>) and  $\alpha$ -quartz-type AlPO<sub>4</sub> <sup>1,42</sup> with  $e_{11} = 0.16$  C/m<sup>2</sup>. However, we are still quite far of the measured values in the langasites such as La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> with <sup>43</sup>  $e_{11} = 0.44$  C/m<sup>2</sup> or the theoretical values predicted <sup>19</sup> in BaZnO<sub>2</sub> ( $e_{11} = 0.72$  C/m<sup>2</sup>).

The decomposition of the piezoelectric-stress elements into an electronic  $(e^{el})$  and a phonon-mediated  $(e^{ph})$  contribution is also reported in Table 6. These two contributions have the same magnitude and opposite sign in the case of the  $e_{11}$ ,  $e_{41}$  and  $e_{51}$  elements, yielding to small overall values. For the  $e_{13}$  and  $e_{33}$  elements, the electronic contribution is one order smaller in mag-

nitude than the vibrational one. For the  $e_{12}$  element, the electronic contribution is almost zero. Thus, the vibrational contribution strongly dominates the  $e_{12}$ ,  $e_{13}$  and  $e_{33}$  piezoelectricstress response. In particular, phonon modes belonging to the *E*-irreducible representation govern the  $e_{12}$  and  $e_{13}$  responses whereas phonon modes belonging to the *A* representation are at the origin to the  $e_{33}^{ph}$  response. An inspection of the calculated polarity and strain coupling for each phonon mode shows that all modes belonging to a same irreducible representation contribute without strong dominance.

The phonon-mediated contribution can also be analyzed from the polyhedron representation. The contribution of each independent polyhedron P(X) to  $e^{ph}$  has been estimated as<sup>44</sup>:

$$e_{j\alpha}^{ph}[P(X)] = e_{j\alpha}^{ph}(X) + \frac{1}{f} \sum_{O \in P(X)} e_{j\alpha}^{ph}(O),$$
 (6)

where  $X = \{La, Na, S_1, S_1'\}$  and f is an integer number given the number of polyhedra sharing the same oxygen atom. This number is equal to 3 for all oxygen except the water oxygens where f = 2. We do not consider that the water molecules are included in the P(La) polyhedra. Thus, their contributions are given by:

$$e_{j\alpha}^{ph}[water] = \frac{1}{2}e_{j\alpha}^{ph}(O_{5w}) + e_{j\alpha}^{ph}(H_1) + e_{j\alpha}^{ph}(H_{1'}).$$
 (7)

The atom-contribution,  $e_{j\alpha}^{ph}(\kappa)$ , of a  $\kappa$ -atom in the unit cell is obtained according to<sup>44</sup>:

$$e_{j\alpha}^{ph}(\kappa) = \frac{1}{\Omega_0} \sum_{\beta} Z_{\alpha\beta}^*(\kappa) \frac{du_{\beta}(\kappa)}{d\eta_j}$$
(8)

where  $du/d\eta$  is the displacement-response internal-strain that describes the first-order displacements resulting from a first-order strain. Results of this projection are shown in Table 7 for the independent elements of  $e_{j\alpha}$  whose the values are the highest. We do not observe a clear dominance of the polyhedral contributions for  $e_{12}^{ph}$ . However, their sign shows that the P(S<sub>1</sub>') polyhedra lead to decrease the overall piezoelectric response. In contrast to  $e_{12}^{ph}$ , the P(La) and P(S<sub>1</sub>) polyhedra dominate  $e_{13}^{ph}$ . Their share the same sign, which is the most favorable situation. The polyhedra centered on the sulfur atoms dominate  $e_{33}^{ph}$ . However, the situation is less favorable than in the previous case as the P(S<sub>1</sub>') response is counterbalanced in part by the P(S<sub>1</sub>) polyhedra. The piezoelectric response of the structural water is small (~0.02-0.04 C/m<sup>2</sup>) and it does not contribute to significatively increase an element of the piezoelectric-stress tensor.

In contrast to the piezoelectric-stress, the knowledge of the piezoelectric-strain is more suitable for potential applications. For example, this quantity estimates the magnitude of the piezoelectric response in an actuator. It can be calculated as: <sup>45</sup>,

$$d_{j\alpha} = \sum_{k} S_{jk}^{(\mathscr{E})} e_{k\alpha} \tag{9}$$

where  $S^{(\mathcal{E})}$  is the elastic compliance tensor defined under the condition of fixed (vanishing) electric field. The full elastic tensor in the P3<sub>1</sub> phase has seven independent elastic constants:  $C_{11}^{(\mathcal{E})}$ ,  $C_{12}^{(\mathcal{E})}$ ,

Polyhedron	$e_{12}^{ph}$	$e_{13}^{ph}$	$e^{ph}_{33}$
P(La)	-0.046	-0.071	-0.056
P(Na)	-0.098	+0.0356	-0.0225
$P(S_1)$	-0.036	-0.101	+0.2385
$P(S_{1'})$	+0.083	-0.026	-0.309
water	-0.038	+0.022	+0.036

Table 7 Calculated vibrational contribution  $(e^{ph})$  of each polyhedron P(X) in the P3<sub>1</sub> phase of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. Values are given in C/m<sup>2</sup>. P(X) is the polyhedron centered on the X-atom (see text). Water labels the strutural water.

Index	$C^{(\mathscr{E})}$ (GPa)	$S^{(\mathscr{E})}$ (TPa $^{-1}$ )
11	73.78	17.73
12	30.57	-5.75
13	29.42	-4.25
14	2.32	-2.49
15	1.20	-1.29
33	82.89	15.08
44	21.86	44.43

Table 8 Calculated elastic  $(C^{(\mathscr{E})})$  and compliance  $(S^{(\mathscr{E})} = [C^{(\mathscr{E})}]^{-1})$  constants defined under the condition of fixed (vanishing) electric field in the P3<sub>1</sub> phase of NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O.

 $C_{13}^{(\mathscr{E})}$  ,  $C_{14}^{(\mathscr{E})}$  ,  $C_{15}^{(\mathscr{E})}$  ,  $C_{33}^{(\mathscr{E})}$  and  $C_{44}^{(\mathscr{E})}.$  These constants are listed in Table 8 and satisfy the Born stability inequalities <sup>46</sup> for the trigonal space group, which indicates that this structure is mechanically stable. The independent elements of the piezoelectric-strain tensor are listed in Table 6. The consideration of the elastic compliances changes most of the tendencies previously discussed on the piezoelectric-stress tensor. Indeed, the highest values (~3.3 pC/N) of the piezoelectric-strain are now observed for the (1,2) and (1,4)-elements. The high value of  $d_{14}$  is related to the high value of S<sub>44</sub>. The value of the other independent elements are about 1 pC/N. The shear  $d_{41}$  value is about five times higher than that measured on  $\alpha$ -quartz ( $d_{41} = 0.73$  pC/N)<sup>2</sup> or predicted on BaZnO<sub>2</sub> ( $d_{41} \sim 0.67$  pC/N)<sup>19</sup>. However, this value is similar with that reported on the La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> lagasite<sup>16</sup> ( $d_{41} \sim 4.5$  pC/N). The  $d_{22}$  value cannot be compared to these coumpounds as it is zero by symmetry in a 32-point group. However, we can compared to the  $d_{11}$  which is also a longitudinal mode. The  $d_{22}$  value of the P3<sub>1</sub> phase in NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O is slightly higher than in  $\alpha$ -quartz ( $d_{11} = 2.31 \text{ pC/N}$ )<sup>2</sup> but about twice smaller than in lagasite<sup>16</sup> ( $d_{11} \sim 6.5$  pC/N). We are also far from the predictions for BaZnO<sub>2</sub>  $(d_{11} = 11.84 \text{ pC/N})^{19}$ .

#### 5 Conclusions

In this article, we reported the existence in NaLa( $SO_4$ )<sub>2</sub>.H<sub>2</sub>O of a displacive phase transition at 200 K from the nonpolar P3<sub>1</sub>21 to the polar P3<sub>1</sub> space groups combining first based calculations and experiments (infrared spectroscopy and x-ray diffraction). Our calculations highlighted the existence of two distinct unstable phonon modes in this P3<sub>1</sub>21 space group. The condensation of these unstable mode allows to determine the phase transitions toward the compatible subgroups using symmetry considerations. Among them, we identified the polar  $P3_1$  as the most probable subgroup according to energy criterion. Then, infrared spectroscopy and x-ray diffraction experiments supported these predictions. Infrared measurements showed the existence of a phase transition at 200 K and the  $P3_1$  space group was identified by x-ray diffraction. The mechanism of this phase transition has been explained from symmetry-adapted distortion modes. The structural water and hydrogen bonding are the mechanism driven the phase transition. The  $A_2$  polar irreducible representation is the primary order parameter. This representation is also responsible of the polar character of the transition.

The piezoelectric properties of this new P3<sub>1</sub> phase have been investigated by first principles based calculations. The six independent piezoelectric-stress constants (e11, e12, e13, e33, e41 and e<sub>51</sub>) have been calculated. The highest piezoelectric-stress values are observed for the  $e_{12}$ ,  $e_{13}$  and  $e_{33}$  with about -0.13 C/m<sup>2</sup>. We discussed microscopic origin of these constants from the analysis of their electronic and the vibrational contributions. We found that the phonon-mediated contribution is the dominant contribution. The vibrational contribution has been also analyzed from the contribution of the different polyhedra used as building blocks in the NaLa( $SO_4$ )<sub>2</sub>.H<sub>2</sub>O structure. The elastic compliance tensors have been calculated and we derived the piezolectric-strain constants. The highest values in the zero Kelvin limit are predicted for  $d_{12}$  and  $d_{41}$  with  $\sim$ 3.4 pC/N. These values are between those observed in  $\alpha$ -quartz and  $\alpha$ -GaPO<sub>4</sub> which is commonly used in piezoelectricity. Thus, NaLa(SO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O could be a potential candidate for piezoelectric application in the low temperature range (below 200 K).

#### Conflicts of interest

There are no conflicts to declare.

#### Acknowledgements

Infrared experiments were performed on the IR-Raman technological platform of the University of Montpellier.

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