

# Reinvestigation of the Phase Transition in ABW-Type CsLiSO<sub>4</sub>: Symmetry Analysis and Atomic Distortions

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ABW-type CsLiSO<sub>4</sub> shows a reversible structural phase transition at approximately 202 K. The transformation is translationengleich and the space group symmetries of the two different polymorphic forms are *Pnma* (phase I) and *P<sub>n</sub><sup>2</sup><sub>1</sub>11* (phase II), respectively. The transition was reinvestigated using a group theoretical approach based on the published structural data of the two modifications. A combined rotation of the SO<sub>4</sub> and LiO<sub>4</sub>-tetrahedra was taken as the primary order parameter  $\eta$  inducing the transformation. Projection operator calculations revealed that the transition can be associated with the irreducible representation  $\Gamma_3^+$  of *Pnma*. Displacements of the Li, S, and Cs ions as well as the occurrence of certain strain components are symmetry allowed, too, and can couple to  $\eta$ . The global tilting pattern is compared with the rotational distortions observed in the transitions of ABW-type CsZnPO<sub>4</sub>. A rigid-unit mode approach is proposed for the explanation of the transitions. © 1998

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## INTRODUCTION

The ABW type of the zeolite nomenclature of Meier and Olson (1) has been investigated frequently. To date, more than 70 different compounds with the ABW-type topology have been compiled (2). The main reasons for the structural studies have been the interesting ferroelectric and ferroelastic effects observed in these materials and, to a lesser extent, the catalytic, ion exchange, or molecular sieve properties usually investigated in microporous zeolite structures.

The highest topological space group symmetry of the ABW framework is *Imma*. This aristotype is identical with the so-called *Icmm* type, a classification which is more commonly used in the mineralogically orientated literature to describe stuffed framework structures (3). The characteristic structural feature of the ABW type is sheets of six-membered rings of tetrahedra with the sequence UUDDDD of up-pointing and down-pointing vertices in one ring.

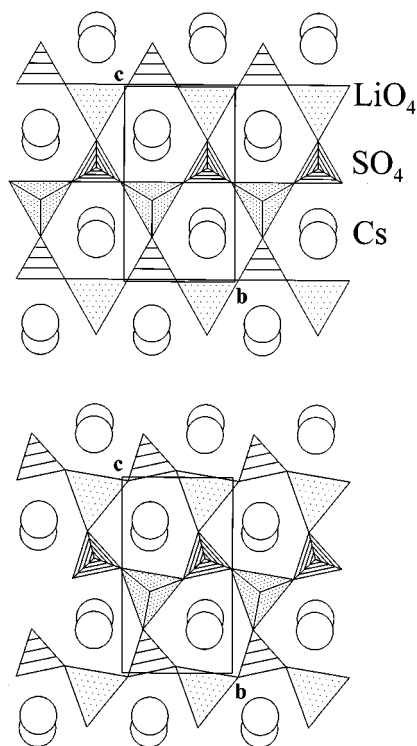
Cesium lithium sulfate also belongs to the ABW family. Kruglik *et al.* (4) as well as Asahi and Hasebe (5) investigated the crystal structure of CsLiSO<sub>4</sub> as a function of

temperature and reported the existence of two different phases upon cooling down from room temperature: An orthorhombic phase I with space group symmetry *Pnma* is stable from room temperature to 202 K ( $a_1 = 8.820(3)$  Å,  $b_1 = 5.456(1)$  Å,  $c_1 = 9.456(2)$  Å,  $Z = 4$ ). The lattice constants refer to 293 K. Below 202 K, the structure transforms to a monoclinic phase II (space group *P<sub>n</sub><sup>2</sup><sub>1</sub>11*;  $a_{II} = 8.834(3)$  Å,  $b_{II} = 5.423(1)$  Å,  $c_{II} = 9.379(2)$  Å,  $\beta = 89.75(2)^\circ$ ,  $Z = 4$ ,  $T = 163$  K).

Each SO<sub>4</sub> tetrahedron in the network of CsLiSO<sub>4</sub> is surrounded by four LiO<sub>4</sub> tetrahedra via common corners and vice versa. The framework contains channels in which the Cs cations are incorporated. Figure 1(top) shows a projection of a single tetrahedral layer parallel to the *a*-axis for the average structure of phase I. The alternating LiO<sub>4</sub> and SO<sub>4</sub> tetrahedra are positioned on mirror planes perpendicular to [010]. In the actual structure, the SO<sub>4</sub> groups are disordered between two orientations symmetric with respect to the mirror plane. On passing through the phase transformation, a rotational ordering occurs and the SO<sub>4</sub> tetrahedra lock in. As a consequence of the ordering, several symmetry elements are lost and the structure becomes monoclinic (compare Fig. 1(bottom)). A comparison of the tetrahedral shapes in the two polymorphic forms reveals that they can be considered as rigid units which are not significantly distorted by the transition. Furthermore, the Cs cations experience only minor changes in their coordinates.

## ORDER PARAMETER DESCRIPTION

In the tables of Stokes and Hatch (7) information is given which is useful for the description of symmetry-breaking phase transitions. The I → II transformation is translationengleich; i.e., there is no multiplication of the primitive cell size at the transition. Therefore, the primary order parameter triggering the transformation has to be associated with a  $\Gamma$ -point representation of *Pnma*. The listing given in Table 1 of ref 7 indicates that the symmetry change to a monoclinic structure with space group symmetry *P<sub>n</sub><sup>2</sup><sub>1</sub>11*



**FIG. 1.** Projection of one network layer parallel to the  $[100]$  direction for the idealized phase I ( $Pnma$ ) (top) and for phase II ( $P_{\pi}^{211}$ ) (bottom) based on the coordinates for 293 and 164 K, respectively, given in ref 4. For drawing of the structural details, the program STRUPLO90 (6) was employed in this paper. Hatched tetrahedra,  $SO_4$  groups; stippled tetrahedra,  $LiO_4$  groups.

can be induced from the onset of an order parameter  $\eta = (a)$  transforming according to the one-dimensional representation  $\Gamma_3^+$ . The image (the set of representation matrices) satisfies the Landau and Lifshitz conditions. Hence, the transformation is allowed to be continuous within both Landau and renormalization theory. Since the transition is classified proper ferroelastic (Aizu species  $mmmF2/m$ ), it is expected that a macroscopic spontaneous strain  $\epsilon_{23}$  could play a significant role in the transition either serving as the primary order parameter or being bilinearly coupled to it. However, for the present discussion of the phase transition, a collective tilting of the tetrahedra is chosen as the primary order parameter.

#### TWIN FORMATION DURING THE PHASE TRANSITION

$P_{\pi}^{211}$  is a maximal subgroup of index 2 of the supergroup  $Pnma$ . Consequently, two domains with the same space group symmetry but with different orientation relative to the high-symmetry  $Pnma$  structure are possible. In Table 1 the orientation and the location of the two domains are listed.

**TABLE 1**  
Domains for Subgroup  $P_{\pi}^{211}$  Arising from the  $\Gamma_3^+$  Irreducible Representation of  $Pnma$

Domain	Direction of $\eta$	Basis	Origin
1	$a$	$(1, 0, 0); (0, 1, 0); (0, 0, 1)$	$(0, 0, 0)$
2	$-a$	$(1, 0, 0); (0, \bar{1}, 0); (0, 0, 1)$	$(0, \frac{1}{2}, 0)$

In the table the following information is given: the domain number, the components of the order parameter for each domain, the lattice basis vectors for the subgroup of that domain, and the subgroup origin relative to the origin of  $Pnma$ . The space groups of both domains are in a well-defined relationship to each other. They are conjugate subgroups relative to  $Pnma$  with the conjugacy element being a symmetry element of  $Pnma$  not contained in  $P_{\pi}^{211}$ . The mirror plane  $1m1$  is not an element of the  $P_{\pi}^{211}$  structure of domain 1. It transforms  $a$  to  $-a$  and gives the conjugate subgroup of domain 2.

#### ROTATIONAL MICROSCOPIC DISTORTIONS

The discussion of the transition to this point has used general symmetry properties associated with the transition: the order parameter transforming according to the irreducible representation  $\Gamma_3^+$ . The subgroup  $P_{\pi}^{211}$  results when  $\eta$  takes the form  $\eta = a$ . The structural analysis revealed that the tetrahedral  $SO_4$  and  $LiO_4$  groups behave as a rigid unit. Assuming a rigid tetrahedron about each S and Li, the primary distortion of the transition is taken to be a rotation of these polyhedra.

The Li and S atoms in phase I as centers of the tetrahedra are located at the  $4(c)$  Wyckoff positions with site symmetry  $1m1$ . The different positions belonging to the  $(c)$  sites,  $(x, \frac{1}{4}, z)$ ,  $(\bar{x} + \frac{1}{2}, \frac{3}{4}, z + \frac{1}{2})$ ,  $(\bar{x}, \frac{3}{4}, \bar{z})$ ,  $(x + \frac{1}{2}, \frac{1}{4}, \bar{z} + \frac{1}{2})$ , will be left unchanged by the respective site symmetry group, a subgroup of  $Pnma$  that is isomorphic to  $m$ . For example, the atom in  $r_0 = (x, \frac{1}{4}, z)$  is invariant under the site group  $\mathcal{L}$  consisting of the elements  $\mathcal{L} = 1m1 = \{(x, y, z); (x, \bar{y} + \frac{1}{2}, z)\}$ . In a manner similar to the way in which lattice modes are calculated, one can assign a local distortion to the  $(x, \frac{1}{4}, z)$  site and then obtain the distortions of other equivalent sites by determining the effects of the symmetry operations of  $Pnma$  that map  $(x, \frac{1}{4}, z)$  onto these points. This process is a well-defined method of group theory and results in an induced representation of  $Pnma$  (8). Depending on the symmetry of the local distortions at the  $4(c)$  sites, only certain space group representations are induced. An induced representation analysis shows that  $\Gamma_3^+$  allows only axial vector distortions at the  $4(c)$  sites about the  $[100]$  and the  $[001]$  directions. Rotations about  $[010]$  are not allowed.

From the assumption that the tetrahedra act as a rigid body, the axial vector contributions can be interpreted as tiltings about the *a* and/or *c* direction.

To analyze the resulting tilting pattern induced by the  $\Gamma_3^+$  representation more precisely, projection operator techniques have to be applied. As described in the paper of Stokes, Hatch, and Wells (9), one can project basis functions  $\psi_i$  of an irreducible representation  $\Gamma^n$  using the basic expression

$$\psi_i = \sum_{g \in \mathcal{G}} D^n(g) g\phi \quad [1]$$

$\phi$  is a local distortion acting at a site  $r_0$  with site symmetry group  $\mathcal{L}$  in the crystal and  $g\phi$  is the corresponding distortion at a site  $gr_0$  equivalent to  $r_0$ .  $g\phi$  can be obtained from  $\phi$  according to  $g\phi = D^{\mathcal{L}}(g)\phi$ . The sum in Eq. [1] is over all elements  $g \in \mathcal{G}$  resulting in the global distortion pattern. The index  $i$  indicates that there is generally more than one independent set of basis functions which can be constructed. The mathematical concepts for the construction of global distortion patterns described briefly in this paragraph have been implemented in the computer program PROJECT (10).

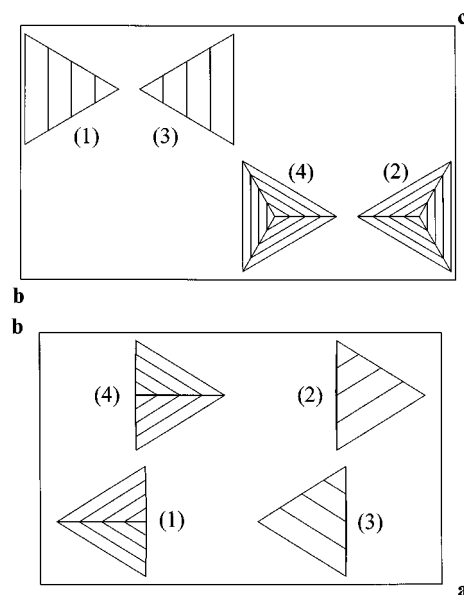
The results of the calculations for the axial vector (rotation) components of the tetrahedra about the centers in Wyckoff 4(*c*) position are shown in Table 2. The distortion gives rotations of equal sense for all four tetrahedra around the S atoms 1–4 about the *a*-axis. On the other hand, for the rotations about the *c*-axis the tetrahedra pairs 1, 2 and 3, 4 show an opposite sense of rotation. Of course, the absolute sign of the rotations as well as the magnitudes  $\Theta_x$  and  $\Theta_z$  for the two rotational degrees of freedom cannot be inferred from a group theoretical approach only. Identical signs in Table 2 indicate a rotation of the same sense. Different signs implicate a rotation in opposite directions.

To compare the derived tilting pattern in Table 2 with the observed rotations in the low-symmetry phase and to show the relationship with the structural model of phase I, the partial structures of the tetrahedra coordinating the four S cations in the unit cells of phase I and phase II are given in Figs. 2 and 3 in projections parallel to the [100] and the [001] directions. The comparison reveals that the actual

**TABLE 2**  
**Axial Vector (Rotation) Mode Components for the 4(*c*)**  
**Wyckoff Site Compatible with the Representation  $\Gamma_3^+$  of  $Pnma^a$**

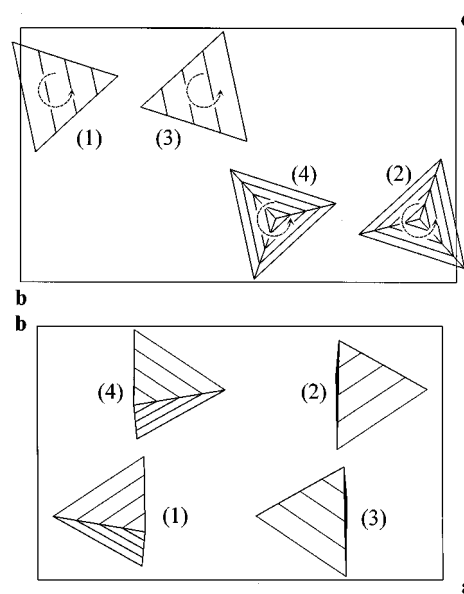
	Point			
Mode	(1) $(x, \frac{1}{4}, z)$	(2) $(\bar{x}, \frac{3}{4}, \bar{z})$	(3) $(x + \frac{1}{2}, \frac{1}{4}, \bar{z} + \frac{1}{2})$	(4) $(\bar{x} + \frac{1}{2}, \frac{3}{4}, z - \frac{1}{2})$
1	$(\Theta_x, 0, \Theta_z)$	$(\Theta_x, 0, \Theta_z)$	$(\Theta_x, 0, \bar{\Theta}_z)$	$(\Theta_x, 0, \bar{\Theta}_z)$

<sup>a</sup>The coordinates refer to the positions of the tetrahedral centers in phase I.



**FIG. 2.** Partial structure of the SO<sub>4</sub> tetrahedra 1–4 inside one unit cell of phase I: (top) projection parallel to [100]; (bottom) projection parallel to [001].

rotation pattern about the *a*- and *c*-axes in phase II is in accordance with the model predicted by the group theoretical approach. The angles of rotation  $\Theta_x$  and  $\Theta_z$  are about 12° and 1°, respectively. The observed tilting pattern for the LiO<sub>4</sub> tetrahedra is also compatible with the theoretical calculations. The rotational configurations for both kinds of



**FIG. 3.** Partial structure of the SO<sub>4</sub> tetrahedra 1–4 inside one unit cell of phase II: (top) projection parallel to [100]; (bottom) projection parallel to [001].

tetrahedra are topologically dependent on each other. For example, a rotation of the  $\text{SO}_4$  tetrahedron 1 in  $(0.204, \frac{1}{4}, 0.083)$  induces an antirotation of the linked  $\text{LiO}_4$  tetrahedron in  $(0.331, \frac{1}{4}, 0.416)$  and vice versa. The tilts of the tetrahedra around the lithium ions are  $\Theta_x = 9^\circ$  and  $\Theta_z \approx 0^\circ$ , slightly lower than for the  $\text{SO}_4$  groups. The values for the rotation angles refer to 202 K, the temperature where the data collection for phase II was accomplished.

The considerations of the last paragraph based on the assumptions that (1) an order parameter leads to the subgroup  $P_{\frac{2}{7}}^2 11$  and (2) the transition is induced by a tetrahedral tilting around the  $4(c)$  sites of  $Pnma$  predict a correct description of the transition. It is not possible, however, to predict the absolute sense of the rotations.

### ADDITIONAL DISTORTIONS CONTRIBUTING TO THE TRANSITION

Up to this point, the symmetry analysis of the transition has been focused on the discussion of the tetrahedral rotational modes transforming according to the  $\Gamma_3^+$  irreducible representation. Using the formalism of induced representation analysis once again, it becomes clear that only polar vectors parallel to the  $b$ -axes are basis functions, too. Therefore, displacements of the tetrahedral centers parallel to the  $[010]$  direction are also symmetry allowed. The results of the projection operator calculation are given in Table 3. Within the atoms belonging to the  $4(c)$  site, the groups 1, 4 and 2, 3 having opposite signs in the local distortion of type  $(0, \delta, 0)$  can be distinguished. These considerations apply not only to the tetrahedral centers but also to Cs atoms in the channels of the tetrahedra which occupy a  $4(c)$  Wyckoff position, too.

A comprehensive description of the distortions at the transition associated with the  $\Gamma_3^+$  representation would consist of contributions from the rotational mode and the displacement mode of the tetrahedral framework and from the displacements of the cations in the channels as well. The amount of each individual contribution cannot be determined from symmetry arguments only.

**TABLE 3**  
**Polar Vector (Displacement) Mode Components for the  $4(c)$  Wyckoff Site Compatible with the Representation  $\Gamma_3^+$  of  $Pnma$**

	Point			
Mode	(1) $(x, \frac{1}{4}, z)$	(2) $(\bar{x}, \frac{3}{4}, \bar{z})$	(3) $(x + \frac{1}{2}, \frac{1}{4}, \bar{z} + \frac{1}{2})$	(4) $(\bar{x} + \frac{1}{2}, \frac{3}{4}, z - \frac{1}{2})$
1	$(0, \delta, 0)$	$(0, \bar{\delta}, 0)$	$(0, \bar{\delta}, 0)$	$(0, \delta, 0)$

<sup>a</sup>The coordinates refer to the positions of the tetrahedral centers in phase I.

### SECONDARY ORDER PARAMETERS

The complete analysis of the phase transformation has to include the discussion of possible secondary order parameters  $q$ . The occurrence of  $q$  results in additional local distortions but does not further reduce the space group symmetry. The distortions are not associated with the irreducible representation  $\Gamma^q = \Gamma_3^+$  but with other representations  $\Gamma^q$  of  $Pnma$ . The condition if an irreducible representation has to be considered when searching for secondary order parameters can also be formulated with the help of subduction frequency calculations (11). Using the relations given in this paper, it becomes obvious that in the actual case only the totally symmetrical irreducible representation of  $Pnma$ ,  $\Gamma_1^+$ , has to be taken into consideration. Certain strain components transform according to  $\Gamma_1^+$ . Specifically, the strain combination  $(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})$  transforms according to this representation. Thus, a volume expansion or contraction can appear at the transition in addition to the ferroelastic strain component  $\varepsilon_{23}$ .

### DISCUSSION

The existence of phase transitions is a phenomenon quite often encountered in ABW framework structures. Recently, the transformations in ABW-type  $\text{CsZnPO}_4$  have been investigated using the same group theoretical approach (12). The present study on the phase transitions in  $\text{CsLiSO}_4$  is a further example of the application of this method. Therefore, it is interesting to compare the results for both cases. For  $\text{CsZnPO}_4$  as well as for  $\text{CsLiSO}_4$ , the symmetry breaking from the high-symmetry modification with space group  $Pnma$  can be attributed to rotations of the tetrahedra located at  $4(c)$  Wyckoff positions about the  $[100]$  and  $[001]$  directions, respectively. The tilting around the  $a$ -axes, perpendicular to the tetrahedral layers containing the six-membered UUDDDD rings, is in both cases definitely more pronounced. The global distortion patterns of the low-symmetry phases of  $\text{CsZnPO}_4$  and  $\text{CsLiSO}_4$  can be explained by the onset of order parameters transforming according to single irreducible representations of  $Pnma$ :  $\Gamma_4^-$  and  $X_2$ , respectively, for the first compound and  $\Gamma_3^+$  for the second compound. In contrast to the transition in  $\text{CsLiSO}_4$ , where each of the four  $\text{SO}_4$  groups in the unit cell has the same rotational sense (about  $[100]$ ), the rotation pattern of the corresponding  $\text{PO}_4$  groups involves antirotations as well. The  $\Gamma_4^-$  representation leading to group symmetry  $Pna2_1$  requires two of the four tetrahedra to rotate in the same direction while the remaining two rotate opposite to the previous.

The displacive phase transitions in  $\text{CsLiSO}_4$  and  $\text{CsZnPO}_4$  show the characteristics of transformations which can be attributed to rigid-unit modes of the idealized ABW-type framework. This vibrational modes can

propagate in a framework structure with no distortion of the tetrahedra, which translate and rotate as rigid units (13, 14). These modes have low frequencies and are therefore candidates for the classical soft modes associated with displacive transformations. Though the lattice dynamical calculations on an ABW-type framework have not been completed, it is very likely that the structural instabilities in CsLiSO<sub>4</sub> and CsZnPO<sub>4</sub> can be linked to rigid-unit modes of the *Pnma* framework.

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