

# Anisotropy in elastic properties of lithium sodium sulphate hexahydrate single crystal—An ultrasonic study

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**Abstract.** The double sulfate family of (ABSO<sub>4</sub>) where A and B are alkali metal cations, is the object of great interest owing to the complexity and richness of its sequence of phase transition induced by temperature variation. A new sulfate salt characterized by the presence of water molecule in the unit cell with the chemical formula, Li<sub>2</sub>Na<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (LSSW), was obtained. The ultrasonic velocity measurement was done with pulse echo overlap technique [PEO]. All the six second order elastic stiffness constants,  $C_{11} = C_{22}$ ,  $C_{33}$ ,  $C_{44} = C_{55}$ ,  $C_{12}$ ,  $C_{14}$  and  $C_{13} = C_{23}$ , are reported for the first time. The anisotropy in the elastic properties of the crystal are well explained by the pictorial representation of the surface plots of phase velocity, slowness, Young's modulus and linear compressibility in  $a$ - $b$  and  $a$ - $c$  planes.

**Keywords.** Inorganic crystal; ultrasonics; elastic properties.

## 1. Introduction

The double sulfate family, (ABSO<sub>4</sub>), where A and B are alkali metal cations, is the object of great interest owing to the complexity and richness of its sequence of phase transition induced by either temperature or hydrostatic pressure variation. The crystals belonging to this family have similar chemical formulae, so they exhibit similar phonon spectra. The crystal, Li<sub>2</sub>Na<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Filho *et al* 1999), belongs to the space group  $C_{3v}^6$  with 6 molecules per unit cell. This belongs to trigonal symmetry and the lattice parameters  $a = b = 8.451$  Å and  $c = 30.28$  Å. The density of the material is measured to be 2.01518 g/cc. Raman studies of this crystal were carried out by Filho *et al* (1999).

Hence the aim of this investigation is to measure the second order elastic constants of LSSW by ultrasonic pulse echo overlap technique and study anisotropy in the elastic properties since no report on elastic properties was available in the literature.

## 2. Experimental

### 2.1 Sample preparation

Li<sub>2</sub>CO<sub>3</sub> and NaHSO<sub>4</sub>·H<sub>2</sub>O was mixed in equi molar ratio in double distilled water. Large crystals of Li<sub>2</sub>Na<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O

(LSSW) was grown by slow evaporation technique at a constant temperature of 308 K. Size of the grown single crystal, LSSW, was (25 × 25 × 30) mm<sup>3</sup>. During growth of this crystal, six crystals were grown at six different temperatures from the same solution. In 323 K, faces [002], [122], [012], [100], [010], [210], [110], [122], [212] and [102] were present. For the crystal grown at 315 K, area of the planes [202], [022], [222] get enlarged. The morphology of certain crystals are different but the morphologies and densities of crystal grown at 313 K, 315 K, 317 K, 319 K and 323 K were almost the same, while crystal grown at 308 K had entirely different morphology and different density. The new sulfate salt was characterized by the presence of water molecule in the unit cell. The presence of water molecule was confirmed by FTIR of this salt as shown in figure 1. The amplitude peak of OH group was at 3431 cm<sup>-1</sup>.

Bulk samples were cut using a slow speed diamond wheel saw so as to have propagation direction along  $a$  and  $c$  axes (Truell *et al* 1969). For trigonal crystal there are three mirror planes. Two parallel cuts are made parallel to one of the mirror plane. Three-fold symmetry planes exist in the [001] plane. A plane parallel to the mirror plane also is cut. With two axes, five of the  $C_{ij}$ 's can be determined. To obtain the sixth elastic constant,  $C_{13}$ , one has to propagate the wave along  $a$ -direction 45° to the  $z$ -axis and in a mirror plane. Faces are identified by measuring interfacial angles and comparing it with that of computed values. The mis-orientation is less than 1°. The sample crystals along the measurement direction are in the range 0.8–1.2 cm. The samples are well polished by using water paper of grade 1500 and cerium

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oxide powder. This enables one to get proper bonding of transducer (figures 2 and 3).

## 2.2 Velocity measurements

The velocity of ultrasonic waves may be determined by measuring sound trip time of plane ultrasonic longitudinal

and transverse waves in the specimen using *X* and *Y*-cut transducers. The ultrasonic velocities are measured using the PEO technique and details of this technique are explained elsewhere (McSkimin 1964; Papadakis 1976). A MATEC model 7700 Pulse modulator and receiver system with its associated subunits have been used for the velocity measurements.

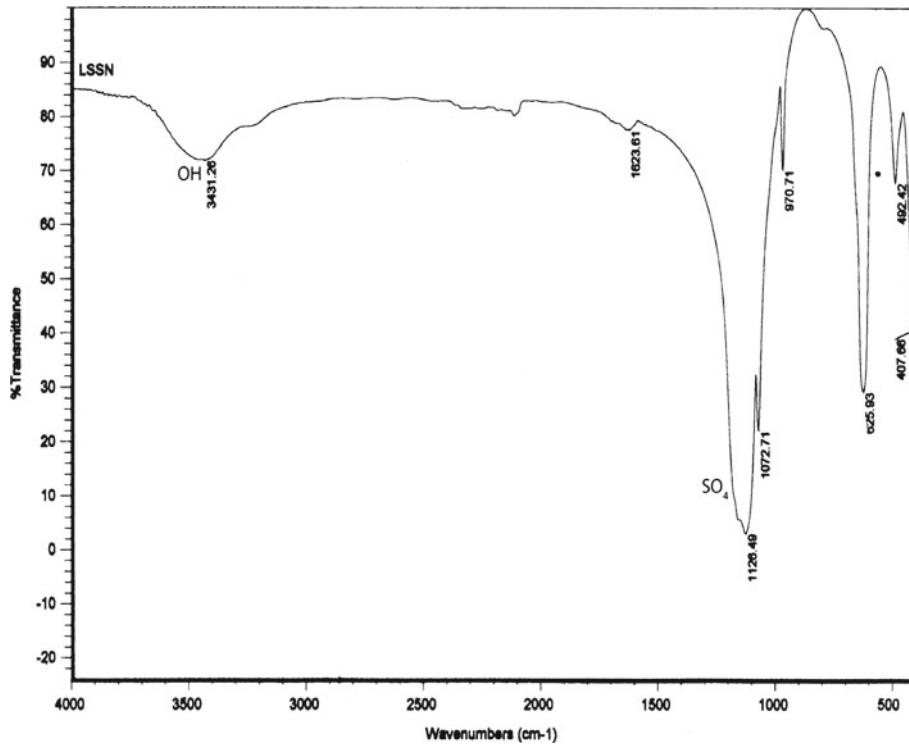


Figure 1. FTIR spectrum of LSSW grown at 308 K.

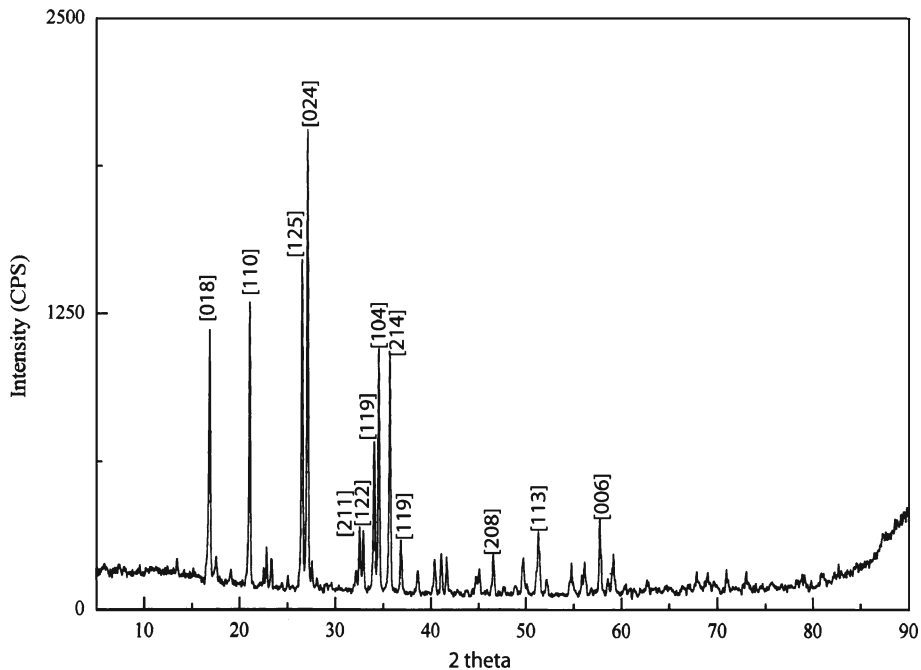


Figure 2. X-ray diffraction pattern of LSSW grown at 308 K.

### 2.3 Elastic constant measurements of trigonal crystal

A rhombohedral crystal has three-fold axis of symmetry and three mirror planes. It is found that  $C_{11} = C_{22}$ ,  $C_{33}$ ,  $C_{44} = C_{55}$ ,  $C_{12}$  and  $C_{14}$  can be obtained by measuring the velocity in  $c$ -direction (three-fold symmetry axis) and any one of the three axes in the base plane normal to a mirror plane and the third pure mode axis in the  $m_1$  plane. The sixth elastic constant,  $C_{13} = C_{23}$ , can be found by velocity measurement of quasi-longitudinal wave in a mirror plane at  $45^\circ$  with  $c$ -axis. The elastic constant,  $C_{66}$ , can be obtained by knowing  $C_{11}$  and  $C_{12}$  by relation.

$\text{Li}_2\text{Na}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (LSSW) can be categorized as type-1 trigonal with 6 independent second order elastic stiffness constants which are  $C_{11} = C_{22}$ ,  $C_{33}$ ,  $C_{44} = C_{55}$ ,  $C_{12}$ ,

$C_{13}$ ,  $C_{14}$  and  $C_{66} = 1/2(C_{11} - C_{12})$ . The constants  $C_{11}$ ,  $C_{33}$  and  $C_{44}$  have been determined from the direct relation,  $C_{ij} = \rho V^2$ , where  $V$  is the relevant sound velocity. Eight velocity measurements enable us to determine all the seven second-order elastic constants. The ultrasonic velocities in these crystals in the specified directions are tabulated in table 1. The values of elastic constants, compliance constants and Poisson's ratios of LSSW grown at 323 K are tabulated in table 3. The elastic constants  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$  and  $C_{66}$  are evaluated from the combination of other elastic constants, with the following cross-checks on the values

$$\begin{aligned} C_{11} > C_{12}; \quad (C_{11} + C_{12}) C_{33} > 2C_{13}^2; \\ (C_{11} - C_{12}) C_{44} > 2C_{14}^2. \end{aligned} \quad (1)$$

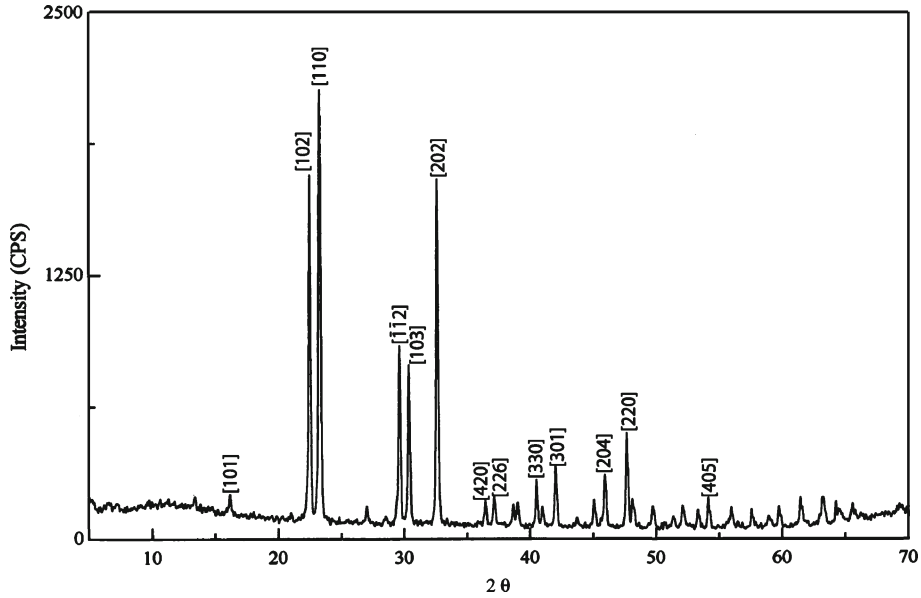


Figure 3. X-ray diffraction pattern of LSSW grown at 323 K.

**Table 1.** Velocity of ultrasonic modes in LSSW at 300 K. L, T, QL, QT represent longitudinal, transverse, quasi-longitudinal and quasi transverse modes, respectively. Relations between mode velocities and elastic constant are also given.

Mode	Direction of propagation	Direction of polan	Measured mode velocity (m/s)	Mode velocity–elastic constant relation
L	[100]	[100]	$V_1 = 4769 \pm 4$	$C_{11} = C_{22} = \rho V_1^2$
T	[100]	[001]	$V_2 = 2592 \pm 2$	$C_{12} = f_{ab}(V_2)$
T	[100]	[001] & [010]	$V_3 = 2628 \pm 2$	$C_{14} = f_{ab'}(V_2 \& V_3)$
L	[001]	[001]	$V_4 = 4808 \pm 4$	$C_{33} = \rho V_4^2$
T	[001]	[100]	$V_5 = 2460 \pm 2$	$C_{44} = C_{55} = \rho V_5^2$
QL	Along mirror plane $45^\circ$ to $c$ axis	QL	$V_6 = 4571 \pm 4$	$C_{13} = f_{ac}(V_6)$

$$f_{ab} = C_{12} = C_{11} + 2C_{44} - 2[\rho v_1^2 + \rho v_2^2], \quad (1)$$

$$f_{ab'} = C_{14} = \frac{1}{2} \left\{ (2\rho v_2^2 - (C_{66} + C_{44})^2 - (C_{66} - C_{44})^2)^{\frac{1}{2}} \right\}, \quad (2)$$

$$f_{ac} = C_{13} = \frac{1}{\sin\theta \cdot \cos\theta} \left\{ \frac{[C - (m^3 - m^2 A + m B)]^{\frac{1}{2}}}{D} \right\} - C_{44}. \quad (3)$$

The off-diagonal constants have been derived from the Christoffel equations (Truell et al 1969) which are given by

$$C_{14} = \frac{1}{2} \left\{ [2\rho v_1^2 - (C_{66} + C_{44})]^2 - (C_{66} - C_{44})^2 \right\}^{1/2}, \quad (2)$$

$$C_{12} = C_{11} + 2C_{44} - 2(\rho v_1^2 + \rho v_2^2), \quad (3)$$

$$C_{13} = \frac{1}{n_3 n_1} \left\{ \left[ \frac{C - (m^3 - m^2 A + m B)}{D} \right] \right\}^{1/2} - C_{44}. \quad (4)$$

Here,

$$C_{11} n_1^2 + C_{44} n_3^2 = a, \quad C_{66} n_1^2 + C_{44} n_3^2 = b, \\ C_{44} n_1^2 + C_{33} n_3^2 = c, \quad 2C_{14} n_1 n_3 = l \rho v_6^2 = m,$$

where  $n_1 = 1/\sqrt{2}, n_3 = 1/\sqrt{2}$  and

$$a + b + c = A, \\ ab + bc + ac - l^2 = B, \\ abc - cl^2 = C, \\ (a - b - 2l) = D. \quad (5)$$

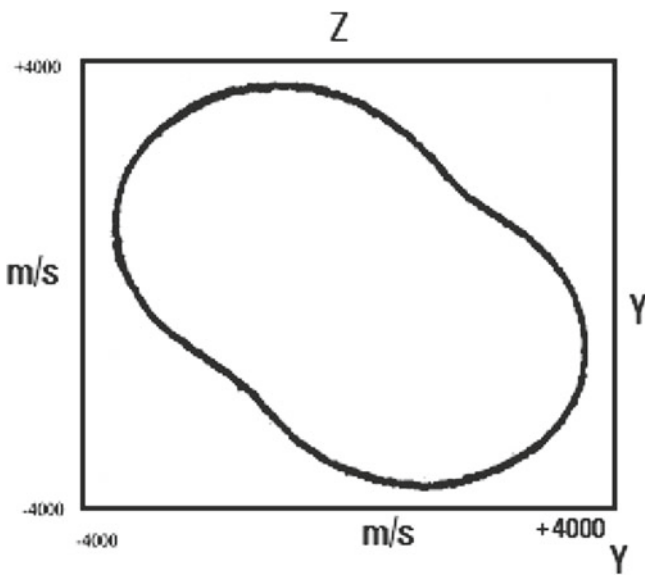


Figure 4. Surface plots of phase velocity for quasi-transverse mode in  $y$ - $z$  plane of LSSW.

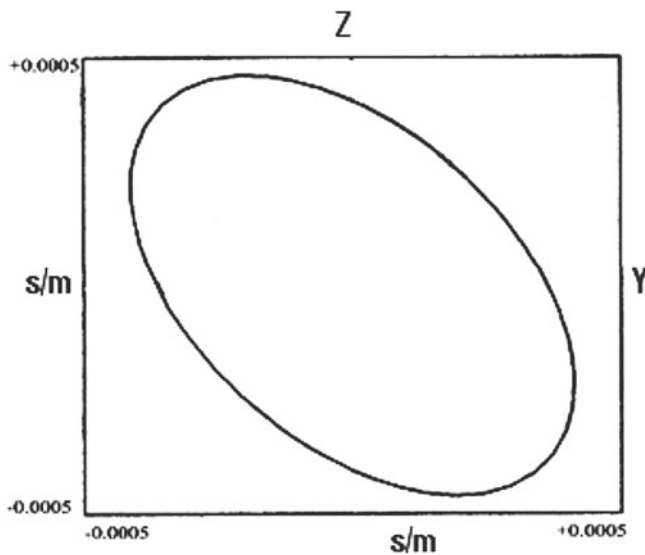


Figure 5. Surface plots of slowness for quasi-longitudinal mode in  $y$ - $z$  plane of LSSW.

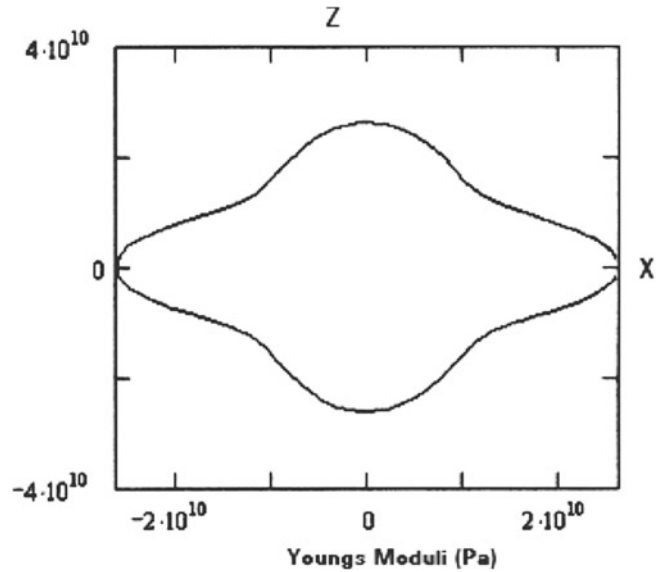


Figure 6. Section of surface of Young's moduli in  $x$ - $z$  plane of LSSW.

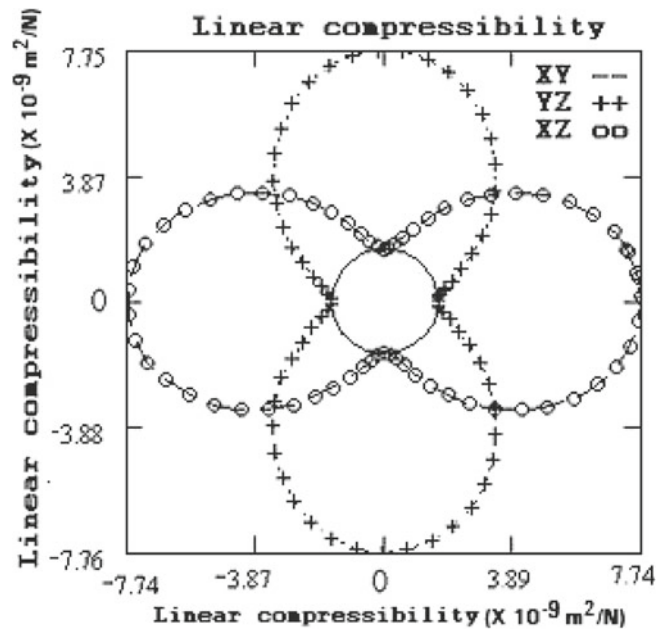


Figure 7. Section of surface of linear compressibility in  $x$ - $y$ ,  $y$ - $z$ ,  $x$ - $z$  planes of LSSW.

**Table 2.** Elastic stiffness constant, compliance constant and Poisson's ratio of LSSW at 300 K.

Sl. No.	Elastic stiffness constant (GPa)	Compliance constant ( $\times 10^{-10} \text{ N}^{-1} \text{ m}^2$ )	Poisson's ratio
1.	$C_{11} = C_{22} = 45.84 \pm 0.09$	$S_{11} = 0.361$	$\nu_{12} = 0.169$
2.	$C_{33} = 46.60 \pm 0.09$	$S_{33} = 0.393$	$\nu_{21} = 0.169$
3.	$C_{44} = C_{55} = 12.21 \pm 0.02$	$S_{44} = S_{55} = 0.845$	$\nu_{13} = 0.417$
4.	$C_{66} = 15.27 \pm 0.03$	$S_{66} = 0.845$	$\nu_{31} = 0.454$
5.	$C_{12} = 15.3 \pm 0.33$	$S_{12} = -0.061$	
6.	$C_{13} = 2.54 \pm 1.2$	$S_{13} = -0.164$	
7.	$C_{14} = 0.648 \pm 0.19$	$S_{14} = -0.225$	

Here,  $n_3 = \cos \theta$ ,  $n_1 = \sin \theta$  and  $\theta$  are measured from  $c$  axis and  $\theta = 45^\circ$ . The diagonal elements can be measured with an accuracy of 0.3% and off-diagonal elastic constants to an accuracy of 1–2.7%.

#### 2.4 Polar plots of phase velocity, slowness, Young's modulus and linear compressibility

The anisotropy in the propagation of elastic waves in this crystal can be illustrated clearly by plotting the phase velocity surface plot in the  $x$ - $z$  plane following the well known procedure (Nye 1957; Alex and Philip 2000). The method involves solution of the Christoffel equations and numerically computing the phase velocity as a function of the direction cosines. Figure 4 shows phase velocity surface, in the  $x$ - $z$  plane, for the ultrasonic wave corresponding to quasi-longitudinal (QT) mode. Polar plots of phase velocity and inverse of phase velocity (slowness) in other planes can also be plotted by following the same procedure and is depicted in figure 5. The velocity surface plots outlined above alone cannot completely describe anisotropy of the elastic properties of a crystal. The Young's moduli surface plots are also very important in this regard. The Young's modulus (Nye 1957; Alex and Philip 2000),  $E$ , in the direction of the unit vector,  $n_i$ , for a trigonal crystal is given by

$$E^{-1} = [1 - n_3^2] S_{11} + S_{33} n_3^4 + [2S_{12} + S_{66}] n_1^2 n_2^2 + n_3^2 [1 - n_3^2] [2S_{13} + S_{44}] + 2n_2 n_3 [3n_1^2 - n_2^2] S_{14}. \quad (6)$$

Here  $S_{ij}$ 's are the respective compliance constants.

The cross-section of Young's modulus surfaces plotted in the  $x$ - $z$  plane is shown in figure 6. The linear compressibility (Nye 1957; Alex and Philip 2000) of a trigonal crystal in the matrix form can be written as

$$\beta = [S_{11} + S_{12} + S_{13}] - [S_{11} + S_{12} - S_{13} - S_{33}] n_3^2. \quad (7)$$

The values of linear compressibility of LSSW crystal in the  $x$ - $y$ ,  $y$ - $z$  and  $x$ - $z$  planes have been (Nye 1957; Alex and

Philip 2000) plotted. These plots are shown in figure 7. The volume compressibility (Nye 1957; Alex and Philip 2000),  $S_{ijkk}$ , is an invariant parameter for a crystal. For the trigonal system, in matrix notation, it is given by

$$S_{iikk} = S_{33} + 2[S_{11} + S_{12} + 2S_{13}]. \quad (8)$$

The value of the volume compressibility of LSSW is obtained as  $0.22 \times 10^{-10} \text{ N}^{-1} \text{ m}^2$  and that of the bulk modulus is 45 GPa.

The Poisson's ratios (Nye 1957) of LSSW are given by the following expressions

$$\begin{aligned} \nu_{21} &= -\varepsilon_{22}/\varepsilon_{11} = -S_{2211}/S_{1111} = -S_{21}/S_{11}, \\ \nu_{31} &= -\varepsilon_{33}/\varepsilon_{11} = -S_{3311}/S_{1111} = -S_{31}/S_{11}, \\ \nu_{12} &= -\varepsilon_{11}/\varepsilon_{21} = -S_{12}/S_{22}, \\ \nu_{13} &= -\varepsilon_{11}/\varepsilon_{33} = -S_{13}/S_{33}. \end{aligned} \quad (9)$$

These have been evaluated and are also tabulated in table 2.

### 3. Results and discussion

Figures 2 and 3 show that the powder X-ray diffraction pattern of LSSW is grown at 308 K and LSS is grown at 323 K. From XRD data it was evident that structure of these two crystals are entirely different. The indexing of XRD proved that the said sample  $\text{Li}_2\text{Na}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  with a space group  $C_{3v}^6$  had 6 molecules per unit cell. This belongs to trigonal symmetry with lattice parameters  $a = b = 8.451 \text{ \AA}$  and  $c = 30.28 \text{ \AA}$ . The indexing of XRD of LSS grown at 323 K has given the lattice parameters as  $a = b = 7.635 \text{ \AA}$  and  $c = 9.86100 \text{ \AA}$ . The above values of lattice parameters of crystals grown at 308 K and 323 K are in close agreement with reported values of LSSW and LSS, respectively. They are compared with JCPDS file card no. 712172. Thus it was proved that the crystal grown at 308 K is not at all LSS but it is another crystal, LSSW, with a different lattice parameter and a space group.

#### 4. Conclusions

A detailed study of the elastic properties of LSSW gives complete set of second order elastic stiffness constants, compliance constants, Poisson's ratios, volume compressibility and bulk modulus of this crystal. All these important parameters for this crystal are measured and tabulated. The elastic anisotropy of various parameters like phase velocity, slowness, Young's modulus and linear compressibility are depicted in the form of two-dimensional surface plots. Some workers (Gundusharma and Seeco 1986; Rao and Sunandana 1996) have erroneously reported crystal grown at 308 K with ingredients  $\text{Li}_2\text{CO}_3$  and  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  as lithium sodium sulphate. Our present results clarify the ambiguity in the structure of this crystal and prove that it actually is  $\text{Li}_2\text{Na}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

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#### References

- Alex A V and Philip J 2000 *Mater. Sci. Eng.* **B90** 241  
Filho J M, Paiva R O, Freire P T C and Melo F E 1999 *J. Raman Spectrosc.* **30** 289  
Gundusharma V M and Seeco E A 1986 *Solid State Commun.* **57** 479  
JCPDS file card no. 712172  
McSkimin H J 1964 in *Physical acoustics Part A* (ed.) W P Mason (New York: Academic Press) **Vol. 1**, p. 271  
Nye N F 1957 *Physical properties of crystals* (London: Oxford University Press) p. 143  
Papadakis E P 1976 in *Physical acoustics* (eds.) W P Mason and R N Thurston (New York: Academic Press) **Vol. XII**, p. 227  
Pina C M, Prieto M and Garcia L L 1995 *J. Cryst. Growth* **148** 283  
Rao S R and Sunandana C S 1996 *Solid State Commun.* **98** 927  
Skoog D A, Holler F J and Nieman T A 1997 in *Principles of instrumental analysis* (Harcourt Asia PTE Ltd) p. 803  
Truell R, Elbaum C and Chick B B 1969 in *Ultrasonic methods in solid state physics* (New York: Academic Press) p. 370  
Walplak S and Krajewski T 1989 *Phys. Status Solidi(a)* **111** 271