

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

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MS received 1 October 2008; revised 22 October 2008

Abstract. The double sulfate family ($ABSO_4$), 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, $Li_2Na_3(SO_4)_2 \cdot 6H_2O$ (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 polar 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 ($ABSO_4$), where A and B are alkali metal cations, is the subject 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, $Li_2Na_3(SO_4)_2 \cdot 6H_2O$ (Filho *et al* 1999), belongs to a space group C_{3v} with 6 molecules per unit cell. This belongs to trigonal symmetry and the lattice parameters $a = b = 8.451 \text{ \AA}$ and $c = 30.28 \text{ \AA}$. The density of the material is measured to be 2.01518 g/cc . Raman studies of this crystal were reported 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 is available in the literature.

2. Experimental

2.1 Sample preparation

Li_2CO_3 and $NaHSO_4 \cdot H_2O$ was mixed in equi molar ratio in double distilled water. Large crystals of Li_2Na_3

$(SO_4)_2 \cdot 6H_2O$ (LSSW) were grown by slow evaporation technique at a constant temperature of 308 K. Size of the grown single crystal, LSSW, was $(25 \times 25 \times 30) \text{ mm}^3$. The same is depicted in figure 1. During the 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], [102] were developed. For the crystal grown at 315 K, area of the planes [202], [022], [222] get enlarged. The morphology of certain crystals were 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 OH dip at 3431 cm^{-1} of FTIR spectrum in figure 4. 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 were three mirror planes. Two parallel cuts were made parallel to one of the mirror planes. Three-fold symmetry planes exist in the [001] plane. A plane parallel to the mirror plane also was cut. With two axes, five of the C_{ij} 's were determined. To obtain the sixth elastic constant, C_{13} , one had to propagate the wave along a -direction 45° to the z -axis, and in a mirror plane. Faces were identified by measuring interfacial angles and comparing with the computed values. The mis-orientation was $< 1^\circ$. The

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sample crystals along the measurement direction were in the range 0.8–1.2 cm. The samples were well polished by using water paper of grade 1500 and cerium oxide powder. This enables one to get proper bonding of transducer.

2.2 Velocity measurements

The velocity of ultrasonic waves was determined by measuring round trip time of plane ultrasonic longitudinal and transverse waves in the specimen using X and Y -cut transducers. The ultrasonic velocities were measured using the PEO technique and details of this technique were 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.

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° with c -axis. The elastic constant C_{66} can be obtained by knowing C_{11} and C_{12} by the relation $\text{Li}_2\text{Na}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. (LSSW) can be categorized as type-I 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



Figure 1. Photograph of lithium sodium sulphate hexahydrate (308 K) and lithium sodium sulphate crystals grown at 313 K, 315 K, 317 K, 319 K and 323 K.

velocities in these crystals in the specified directions are tabulated in table 1. The values of the elastic constants, compliance constants and Poisson's ratios of LSSW grown at 323K are tabulated in table 2. 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.

$$C_{11} > C_{12}; (C_{11} + C_{12})C_{33} > 2C_{13}^2;$$

$$(C_{11} - C_{12})C_{44} > 2C_{14}^2. \quad (1)$$

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

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

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

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

where

$$C_{11}n_1^2 + C_{44}n_3^2 = a, \quad C_{66}n_1^2 + C_{44}n_3^2 = b,$$

$$C_{44}n_1^2 + C_{33}n_3^2 = c, \quad 2C_{14}n_1n_3 = l \quad \rho v_6^2 = m,$$

where

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

$$a + b + c = A,$$

$$ab + bc + ac - l^2 = B,$$

$$abc - cl^2 = C,$$

$$(a - b - 2l) = D. \quad (5)$$

Here $n_3 = \cos\theta$, $n_1 = \sin\theta$, and θ is 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 Jacob 2000). The method involves solution of the Christoffel equations and numerically computing the phase velocity as a function of the direction cosines.

Figure 5 shows the phase velocity surface, in the x - z plane, for the ultrasonic wave corresponding to quasi-

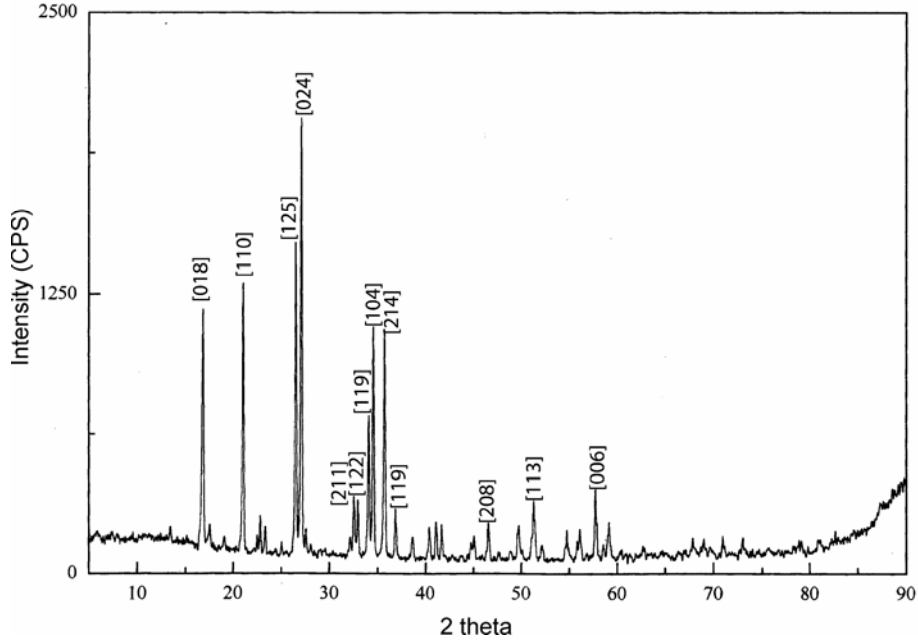


Figure 2. XRD of lithium sodium sulphate hexahydrate [LSSW] crystal.

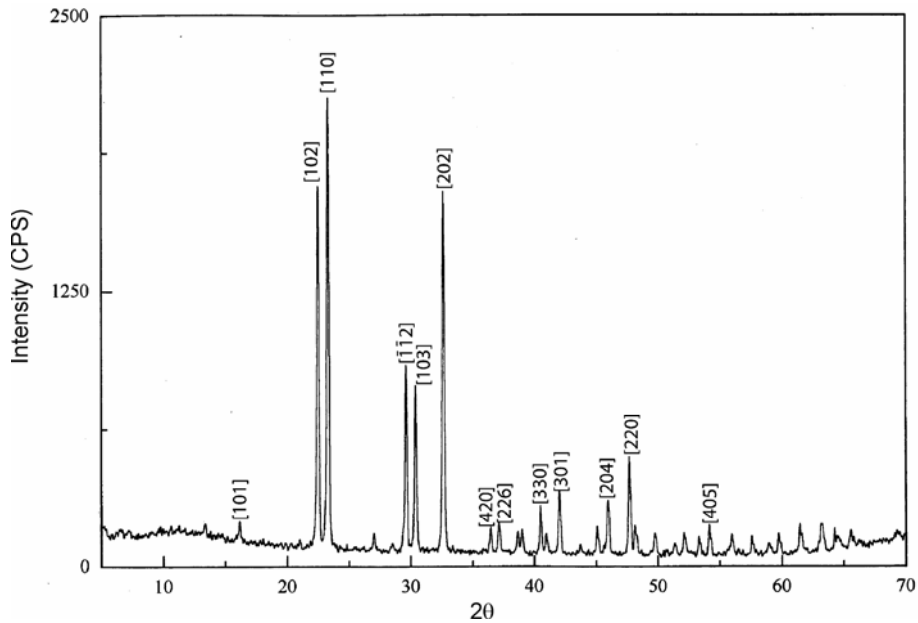


Figure 3. XRD of grown lithium sodium sulphate [LSS] crystal.

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 6. The velocity surface plots outlined above alone cannot completely describe the 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 Jacob 2000), E , in the direction of the unit vector, n_i , for a trigonal crystal is given by

$$E^{-1} = [1 - n_3^2]S_{11} + S_{33}n_3^4 + [2S_{12} + S_{66}]n_1^2n_2^2 + n_3^2[1 - n_3^2][2S_{13} + S_{44}] + 2n_2n_3[3n_1^2 - n_2^2]S_{14}. \quad (6)$$

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 7. The linear compressibility (Nye 1957; Alex and Jacob 2000) of a trigonal crystal in the matrix form can be written as

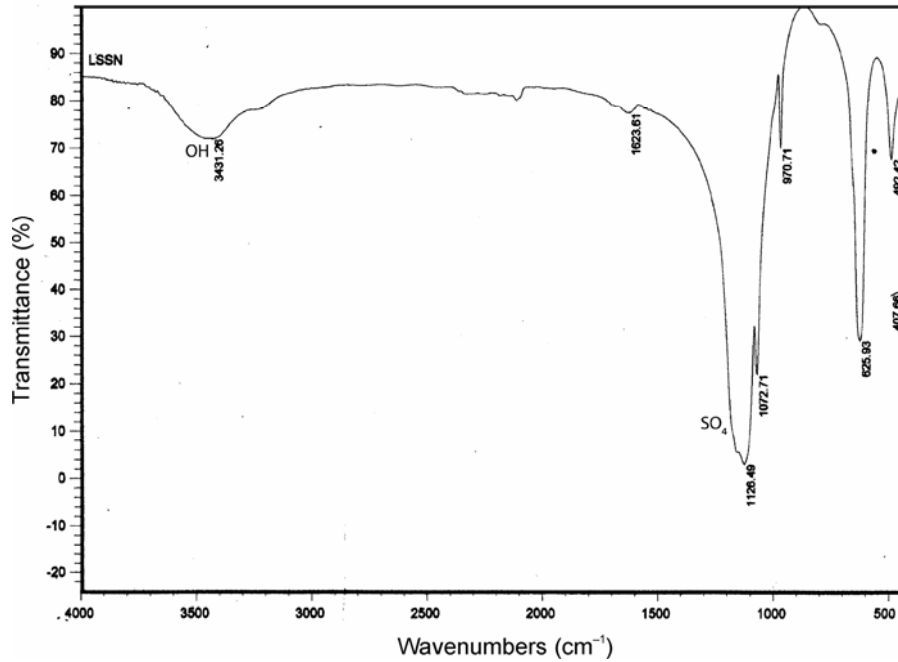


Figure 4. FTIR spectrum of lithium sodium sulphate hexahydrate crystal.

Table 1. Velocity of ultrasonic modes in LSSW at 300 K.

Mode	Direction of propagation	Direction of polarization	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° to <i>c</i> axis	QL	$V_6 = 4571 \pm 4$	$C_{13} = f_{ac}(V_6)$

L, T QL, QT represent longitudinal, transverse, quasi-longitudinal and quasi transverse modes, respectively.

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

The values of linear compressibility of LSSW crystal in the *x*-*y*, *y*-*z* and *x*-*z* planes have been plotted (Nye 1957; Alex and Jacob 2000). These plots are shown in figure 8. The volume compressibility (Nye 1957; Alex and Jacob 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:

$$\nu_{21} = -\varepsilon_{22}/\varepsilon_{11} = -S_{2211}/S_{1111} = -S_{21}/S_{11},$$

$$\nu_{31} = -\varepsilon_{33}/\varepsilon_{11} = -S_{3311}/S_{1111} = -S_{31}/S_{11},$$

$$\nu_{12} = -\varepsilon_{11}/\varepsilon_{21} = -S_{12}/S_{22},$$

$$\nu_{13} = -\varepsilon_{11}/\varepsilon_{33} = -S_{13}/S_{33}. \quad (9)$$

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

3. Results and discussion

A detailed study of elastic properties of the crystal has been reported for the first time. Figures 2 and 3 showed the powder X-ray diffraction pattern of lithium sodium sulphate grown at 308 K and 323 K. From XRD data it was evident that structures of these two crystals are entirely different though they have been grown from the same solution. They have been compared with JCPDS

Table 2. Elastic stiffness constant, compliance constant and Poisson's ratio of LSSW.

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	$C_{44} = C_{55} = 12.21 \times 0.02$	$S_{44} = S_{55} = 0.845$	$\nu_{13} = 0.417$
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	$C_{14} = 0.648 \pm 0.19$	$S_{14} = -0.225$	

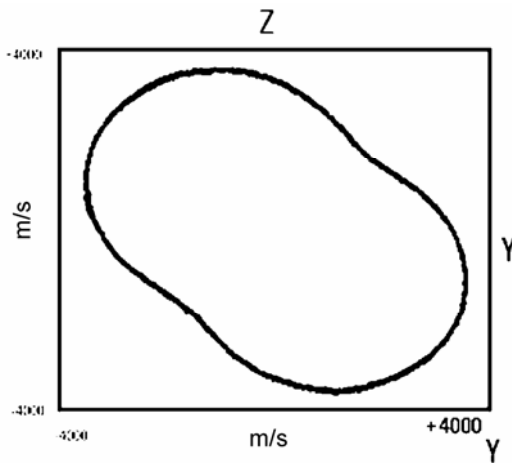


Figure 5. Polar plot of phase velocity.

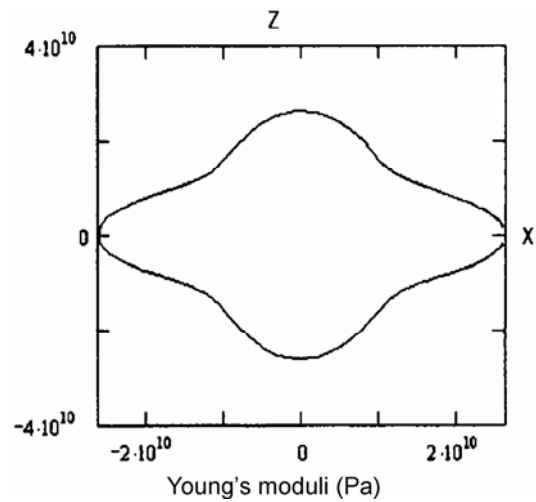


Figure 7. Polar plot of Young's modulus.

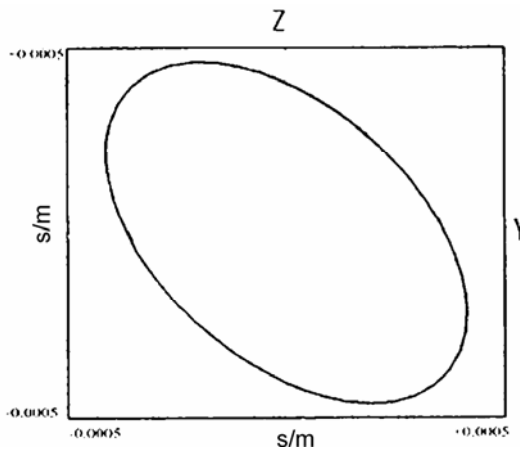


Figure 6. Polar plot of slowness.

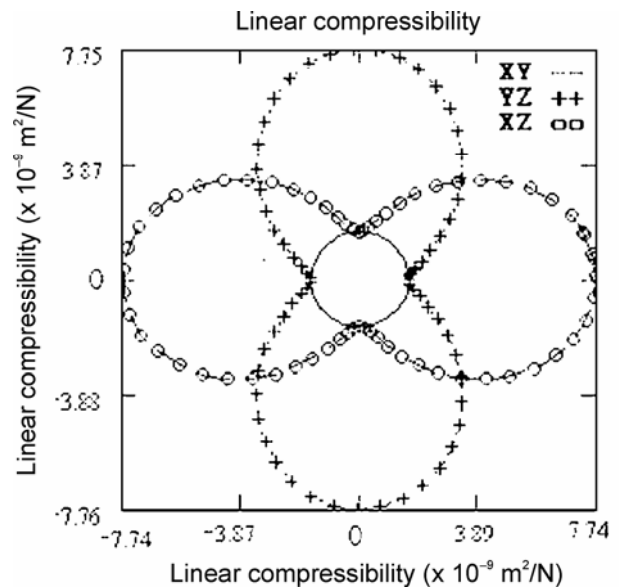


Figure 8. Polar plot of linear compressibility.

file card no. 712172. Thus it was proved that the crystal grown at 308 K is not at all lithium sodium sulphate but it is $\text{Li}_2\text{Na}_3(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with different lattice parameter and space group. Some workers (Rao and Sunandana 1996; Gundusharma and Seeco 1986) have erroneously reported crystal grown at 308 K with ingredients Li_2CO_3 and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ as lithium sodium sulphate.

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. Our present results clarified the ambiguity in the structure of this crystal grown at 308 K.

Acknowledgement

One of the authors (GV) thanks (UGC), Delhi, for a teacher fellowship.

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